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ARL 63-82

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# THE EFFECT OF ADDITIVES ON THE MECHANISM OF DETONATION IN GASEOUS SYSTEMS

*Seal 2*

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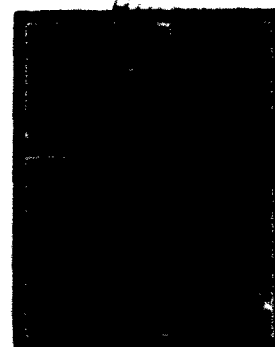
(Presented in partial fulfillment of the requirements for the Degree of Doctor of  
Philosophy in the Graduate School of the Ohio State University, Columbus, Ohio)

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TO:

SUBJECT: Errata and Omissions  
Technical Report ARL 63-82, "The Effect of Additives  
on the Mechanism of Detonation in Gaseous Systems,"  
by Bernard T. Wolfson, Aeronautical Research Laboratories,  
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Force Base, Ohio, May 1963

In Figure 43, page 409, add the appropriate reference numbers  
corresponding to each symbol:

REF: 25,26... 	REF: 264..... 
104..... 	133..... 
126..... 	134..... 
17..... 	82,83... 
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16..... 	225..... 
195..... 	225..... 
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## ABSTRACT

Detonation has caused the destruction of chemical process plants, and is associated with destructive "combustion instability" in present-day propulsion systems. Detonation-type combustion is being considered for use in hypersonic flight propulsion systems and test facilities, manufacture of chemicals, and explosive forming and welding of metals. Most previous work in steady detonation waves in gases was done at or near ambient initial pressure and temperature and mainly involved the influence of initial gas composition on detonation velocity. Only little attention has been given heretofore to the influence of additives on gaseous detonations, especially at high initial pressures.

This dissertation investigates the effect of helium, argon and carbon dioxide additives on the mechanism of detonation in stoichiometric hydrogen-oxygen mixtures over wide ranges of initial pressures and additive concentrations, and attempts to determine the validity of the Chapman-Jouguet thermohydrodynamic theory under these conditions.

No quantitative conclusions can be made about whether complete chemical and/or thermal equilibrium in the Chapman-Jouguet plane was established, or to whether the "frozen" or "equilibrium" product gas sound speed is most correct in the real gas situation. The detonation velocity was slightly dependent on initial pressure but was critically dependent on mixture composition. The experimental detonation static pressures followed the same general trend as the velocities. The theoretical detonation and shock wave pressures and temperatures increased linearly with initial pressure and were relatively independent of mixture composition. Detonation and shock wave pressures and temperatures should be seriously considered in the design of equipment subject to detonation.

No evidence was obtained of the "von Neumann spike" or of an induction zone. The pressure measuring system used did not have sufficient time resolution to detect such highly transient events. The pressure measuring system was not entirely satisfactory. The experimental pressure data presented were qualitative only due to the uncertainty associated with the pressure measurements,  $\pm 20$  to  $\pm 60$  psi. With additional modifications very accurate pressure measurements could have been obtained at rise times of about 0.5 microseconds.

Additives retarded the rate of attainment of stable detonation in stoichiometric hydrogen-oxygen mixtures. The stabilization rate increased with increase in initial pressure and with decrease in additive concentration. The rates appeared to be closely associated with the predetonation lengths, and the deviations between theoretical and experimental values of detonation parameters. Addition of carbon dioxide had the greatest influence and argon the least on these quantities and on the mechanism of detonation in the gaseous mixtures considered.

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## NOMENCLATURE

### SYMBOL

$a$	Speed of sound
$A, B$	Constants
$a''_{\text{eff}}(g)$	"Effective" speed of sound in the final mixture
$A_N$	Number of chemically non-reactive elements involved in the detonation process.
$A_T$	Total number of chemical elements involved in the detonation process.
$A_R$	Number of chemically reactive elements involved in the detonation process.
$C$	Damping coefficient
$C_{P_n}$	Molal heat capacity at constant pressure, <u>not including</u> the effects of the heats of reaction.
$C_r$	Critical damping coefficient
$\left(\frac{C_p}{R}\right)_n$	Dimensionless molal heat capacity at constant pressure, <u>not including</u> the effects of the heats of reaction.
$c_{P_n}$	Specific heat at constant pressure <u>not including</u> the effects of the heats of reaction.
$c_{P_r}$	Specific heat at constant pressure <u>including</u> the effects of the heats of reaction.
$c_{V_n}$	Specific heat at constant volume <u>not including</u> the effects of the heats of reaction.
$c_{V_r}$	Specific heat at constant volume <u>including</u> the effects of the heats of reaction
$d$	Damping ratio ( $2d = C/C_r$ )
$D$	Detonation velocity - velocity of the detonation wave with respect to the initial mixture.

NOMENCLATURE (CONT.)SYMBOL

$\Delta E_0(e)$	Absolute molal zero point energy of any element (e) in its standard state of aggregation at 0°K.
$\Delta E_0^\circ(i)$	Heat of reaction at 0°K for the formation of the i-th component from the elements in their standard states of aggregation at 0°K.
$\left(\frac{\Delta E_0^\circ}{R}\right)_i$	Heat-of-reaction function at 0°K for the formation of the i-th component from the elements in their standard states of aggregation at 0°K
$f_0$	Undamped natural frequency of transducer
$f$	Fugacity
$F(t)$	Driving function acting on transducer diaphragm area ( $F(t) = y$ ).
$F$	Absolute molal free energy
$(F^\circ - E_0^\circ)_i$	Free energy of the i-th chemical component, in its standard state in a mixture at temperature T, relative to its free energy in its standard state at 0°K
$\left(\frac{F^\circ - E_0^\circ}{RT}\right)_i$	Free energy function for the i-th chemical component in a mixture at temperature T.
$h$	Absolute specific enthalpy
$\Delta h$	Absolute specific enthalpy difference
$H$	Absolute molal enthalpy
$H_0^\circ(e)$	Absolute molal enthalpy of any element (e) in its standard state of aggregation at reference temperature 0°K
$(H^\circ - E_0^\circ)_i$	Molal enthalpy of the i-th chemical component in its standard state of aggregation in a mixture at temperature T, relative to its enthalpy at 0°K
$\left(\frac{H^\circ - E_0^\circ}{RT}\right)_i$	Enthalpy function for the i-th chemical component in a mixture at temperature T.

# NOMENCLATURE (CONT.)

xx

## SYMBOL

$\Delta H_{f(i)}$	Heat of formation of the i-th chemical component at temperature T from the elements in their standard states of aggregation at 0°K.
$\left( \frac{\Delta H_f}{RT} \right)_i$	Dimensionless heat of formation of the i-th chemical component at temperature T from the elements in their standard states of aggregation at 0°K.
$I_i$	The chemical symbol for the i-th component in the initial or final mixture.
$k$	Spring constant of transducer's elastic element.
$K_p(j)$ or $K_j$	Equilibrium constant, in terms of partial pressures, for j-th chemical reaction occurring in the final mixture at the final conditions; units are atmospheres raised to the power $i(j) = i(j)$ . (The chemical reaction is the formation of one mole of the specie from the elements in their standard states of aggregation.)
$m$	Molecular mass
$m^*$	Effective mass of transducer
$M'$	Detonation Mach number, i. e., the Mach number of the detonation wave with respect to the initial mixture.
$M''$	Mach number of the detonation wave with respect to the final mixture.
$M_{NS}$	Mach number behind a normal shock wave traveling into the <u>initial</u> mixture at the speed of the detonation wave, <u>with constant specific heats and with no chemical reaction taking place in the shock wave.</u>
$n$	Number of moles
$n_e(i)$	Number of moles of any element (e) involved in the formation of one mole of a chemical component ( $I_i$ ) from its elements in their standard states of aggregation at reference temperature 0°K

NOMENCLATURE (CONT.)

xxd

SYMBOL

$n''_g$	Total number of moles in the gaseous phase in the final mixture.
$n''_i(g)$	Number of moles of the i-th chemical component in the gaseous phase in the final mixture.
$n''_i(s)$	Number of moles of the i-th chemical component in the condensed phase in the final mixture.
$N'$	Number of chemical components in the initial mixture.
$N''$	Number of chemical components in the final mixture.
$N_F(i),$ $N_G(i)$	Number of atoms of elements F, G, respectively, in one molecule of the i-th component in the initial or final mixture (always on integral value or zero).
$p$	Pressure
$p'$	Pressure in the initial mixture (static pressure).
$p''$	Pressure in the final mixture behind the detonation wave (Chapman-Jouguet condition) (static pressure).
$p_C(\text{vap})$	Vapor pressure of carbon (monatomic) at temperature T.
$p''_i$	Partial pressure of the i-th component in the final mixture (static pressure).
$p''_I$	Detonation wave impact pressure.
$p_{NS}$	Pressure behind a normal shock wave traveling into the initial mixture at the speed of the detonation wave, with constant specific heats and with no chemical reaction taking place in the shock wave.
$p_{I(NS)}$	Normal Shock Wave Impact Pressure
$R$	Universal gas constant.
$S$	Absolute molal entropy.

NOMENCLATURE (CONT.)SYMBOL

$\left(\frac{s}{R}\right)$	Entropy function
t	Time
T	Absolute temperature
$T_{NS}$	Temperature behind a normal shock wave traveling into the initial mixture at the speed of the detonation wave, <u>with constant specific heats</u> and with no chemical reaction taking place in the shock wave.
$u' = D$	Velocity of the detonation wave with respect to the initial mixture (i. e., Detonation velocity).
$u''$	Velocity of the detonation wave with respect to the final mixture behind the detonation wave (Chapman-Jouguet condition).
v	Molal volume
V	Volume occupied by n moles of mixture.
$V'$	Total volume occupied by $n'$ moles of initial mixture at $p'$ , $T'$
$V''$	Total volume occupied by $n''$ moles of final mixture at $p''$ , $T''$
$V''_g$	Volume occupied by $n''_g$ moles of final mixture at $p''$ , $T''$
w	Velocity of detonation product gases with respect to wave front ( $w = u' - u''$ ).
$\omega_0$	Angular undamped natural frequency of transducer.
x	Mole fraction.
X	Voltage output of transducer proportional to the displacement of transducer diaphragm.

NOMENCLATURE (CONT.)SYMBOL

$z$	Compressibility factor.
$Z_E$	Maximum number of independent chemical equilibrium equations
$Z_M$	Maximum number of independent mass balance equations, in terms of partial pressures

GREEK SYMBOLS

$\gamma_{\text{eff}}(g)$	"Effective" specific heat ratio for the final gaseous mixture ("effective" $\gamma$ ).
$\gamma_n$	Specific heat ratio (or molal heat capacity ratio), not including the effects of the heats of reaction ("non-reacting" $\gamma$ ).
$\gamma_r$	Specific heat ratio <u>including</u> the effects of the heats of reaction ("Reacting" $\gamma$ ).
$\nu_{i(j)}$	Stoichiometric mole number of the $i$ -th component in the $j$ -th chemical reaction, positive for the products and negative for the reactants.
$\Delta \nu_{i(j)}$	Change in stoichiometric mole number for the $j$ -th chemical reaction.
$\rho$	Density
$\rho_{NS}$	Density behind a normal shock wave traveling into the initial mixture at the speed of the detonation wave, with constant specific heats and with no chemical reaction taking place in the shock wave.
$\Sigma$	Symbol indication summation.

SUBSCRIPTS

$\bullet$	Pertaining to any chemical element.
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NOMENCLATURE (CONT.)SUBSCRIPTS (cont.)

<b>f</b>	Pertaining to a formation reaction starting with the elements in their standard states of aggregation (Standard states of the elements are taken to be solid carbon, as pure graphite, or $C_{(s)}$ ; $O_2$ , $H_2$ , He and A as ideal gases at 1 atm. pressure).
<b>F, G</b>	Pertaining to any two atomic species F and G, respectively.
<b>g</b>	Pertaining to gaseous component(s) only.
<b>i</b>	Pertaining to the i-th chemical component in a mixture.
<b>j</b>	Pertaining to the j-th chemical reaction.
<b>l</b>	Pertaining to the l-th chemical reaction.
<b>n</b>	Signifies that the effects of heats of reaction <u>are not included</u> .
<b>N</b>	Pertaining to chemically non-reactive elements involved in the detonation process.
<b>NS</b>	Pertaining to a normal shock wave traveling into the initial mixture at the speed of the detonation wave.
<b>o</b>	Pertaining to the state condition 0°K.
<b>p</b>	Pertaining to constant pressure.
<b>r</b>	Signifies that the effects of heats of reaction <u>are included</u> .
<b>rs</b>	Pertaining to the reaction zone.
<b>R</b>	Pertaining to chemically reactive elements involved in the detonation process.
<b>s</b>	Pertaining to component(s) in the condensed phase.

## NOMENCLATURE (CONT.)

xxv

### SUBSCRIPTS (cont.)

- T**                    Pertaining to total number of chemical elements involved in the detonation process.
- v**                    Pertaining to constant volume.

### RIGHT SUPERSCRIPTS

- (<sup>o</sup>)** (Degree sign) Pertaining to the standard state (for gases, ideal gas at 1 atmos. pressure, i. e.,  $f^o = p^o = 1$ ; for solid carbon, pure graphite).
- (<sup>'</sup>)** (Prime) Pertaining to conditions (state properties or composition) in the initial mixture.
- (<sup>''</sup>)** (Double Prime) Pertaining to conditions (state properties or composition) in the final mixture behind the detonation wave (Chapman-Jouguet condition).

## I. INTRODUCTION

Since 1881, (19, 213) it has been recognized that two different types of reaction waves can exist in gaseous substances capable of exothermic reaction. Subsequent investigations have revealed that the velocity characteristics of each type of wave is controlled by entirely different mechanisms. The first type, now generally called a deflagration wave, or ordinary combustion, is characterized by a relatively slow moving flame front traveling into the unburned gas at subsonic velocity, normally on the order of several feet per second. The velocity of propagation of the flame front is controlled by molecular transport properties of the gas, viscosity, diffusion and/or thermal conductivity, and upon detailed chemical kinetics of the combustion process. Its motion is markedly influenced by compression and rarefaction waves created by the reaction and by reflection from open or closed boundaries of the containing vessel. (2, 88, 110, 169, 176, 185, 194, 216, 320).

The second type of reaction wave, called a detonation wave, is characterized by its supersonic rate of propagation (3,000 to 12,000 feet/sec.) with respect to the undetonated gas, accompanied by large pressure and temperature increases across the wave. The detonation wave occurs from the deflagration wave under certain conditions of confinement and gas composition. During this transition period the

rate of propagation adjusts rapidly from the initially slow-moving deflagration wave to a constant supersonic value. The influence of chemical kinetics of the combustion reaction, mass diffusion, viscosity and thermal conductivity normally are of minor significance for the steady detonation. A successful theory of steady detonation waves exists: the so-called "Chapman-Jouguet thermohydrodynamic theory" (46, 70, 71, 171, 172, 173). This theory treats the detonation waves from a thermohydrodynamic view point, disregarding finer kinetic and chemical details. Thus it is concerned with the macroscopic properties of the detonation wave only. (See also Literature Review, Section II-D.)

The study of supersonic energy release or the phenomenon of detonation is important from both an academic and a practical viewpoint. A number of research facilities, e. g., large research shock tubes (113, 150, 209, 227, 262, 268, 269), and chemical processes involve initial reactants and/or final gaseous products which are capable of detonating. Some of these processes and facilities are operated at high initial pressures and temperatures. Detonation in the past has caused tremendous destruction in a number of these installations (164, 241, 259, 288, 300, 315). Detonation is believed by many to be closely associated with destructive "combustion instability" in present-day propulsion systems and in other chemical reactors (6, 21, 26, 69, 80, 109, 236, 255, 256, 274, 275, 310, 315, 324). This instability phe-

phenomenon is one of the main factors which limits the satisfactory "scaling-up" of present-day rocket propulsion systems to the large sizes required for advanced terrestrial missile and space-flight vehicles. Consideration is also being given to advantageous application of detonation to advanced air-breathing hypersonic flight propulsion systems (96, 93, 124, 140, 141, 142, 233, 242, 263, 272, 273, 276, 305, 307) and hypersonic high-pressure high-temperature combustion test facilities (142, 272, 315), and to explosive forming (563) and welding (74) of metals.

A complete understanding of the basic chemical and gas dynamic processes occurring in detonation phenomenon is required as a necessary first step to the proper evaluation of the advantageous application of detonation to propulsive and other devices discussed above. Also intimate knowledge of the destructive forces associated with detonation, calculatable on a priori basis from the known properties of a hypothetical detonable gaseous mixture, is a necessity for the engineer concerned with the structural design, reliability, safety and operation of reactors, chemical process equipment, propulsion systems and research tools discussed above, where gaseous mixtures capable of detonating are involved.

A great deal of experimental and theoretical work has been done in the field of gaseous detonation since its recognition some eighty

years ago. Much progress has been made in understanding and explaining the detonation phenomenon from both a macroscopic and microscopic viewpoint. However, much work remains to be done before we can claim to have a completely satisfactory fundamental understanding of detonation phenomenon. (See Literature Review, Section II for details.)

Detonation wave velocities have been studied far more extensively than any other detonation property, since they are the easiest to obtain. Until recently the majority of gaseous detonation studies were limited to the determination of the influence of initial gas composition on the wave velocity at ambient or relatively low initial pressures and ambient temperatures. Very little attention has been given to the influence of additives on the detonation parameters and on the mechanism of detonation. Previous studies in this area were with inert additives, such as helium and argon, to determine whether the density or molecular weight effect on the detonation velocity agreed with the theoretical value predicted by the Chapman-Jouguet theory. These previous studies, unfortunately, were confined to ambient initial temperature and initial pressures below 2 atmos. Very little data was found in the literature on the influence of an additive, such as carbon dioxide, which can act as a pure diluent or as a chemically reactive constituent under the proper conditions.

In contrast to detonation wave velocity measurements, only a very small number of detonation pressure or density measurements have been made. Also these measurements were confined to ambient initial temperature and ambient or low initial pressure. The pressure measurements, for the most part, are of doubtful accuracy. No experimental and very little theoretical detonation wave pressure or density data was found in the literature for gaseous mixtures at high initial pressures. Only little attention has been placed on the influence of initial pressure and/or temperature on the values of the detonation parameters and on the mechanism of detonation. Close agreement has been found between experimental and calculated values based on the classical Chapman-Jouguet theory for many low pressure gaseous detonations. However, none of the various postulated models of detonation, in particular the von Neumann-Döring-Zeldovich model, or the Chapman-Jouguet theory has been thoroughly tested, and the detonation and shock front properties have not been determined over wide ranges of initial pressure and temperature in gaseous detonable mixtures, with or without additives. In particular, the high pressure region has been virtually unexplored; i. e., above 2 atmospheres initial pressure.

The main purpose of the present investigation was to extend the range of the study of detonation phenomena in gaseous mixtures, with and without additives, over a much wider range of initial pressures

than heretofore reported, and to determine the validity of the Chapman-Jouguet thermohydrodynamic theory under these conditions. By this means, it was believed that additional fundamental understanding of the mechanism and fluid dynamics of supersonic energy release or detonation in gaseous mixtures could be obtained. This was accomplished by investigating both experimentally and theoretically the influence of helium, argon, and carbon dioxide on the mechanism of detonation in stoichiometric hydrogen-oxygen mixtures over a wide range of initial pressures and additive concentrations. Detonation velocities and static pressures were measured in these mixtures at initial pressures from 1/2 to 50 atmospheres and additive concentrations from 0 to 50 per cent by volume. Theoretical Chapman-Jouguet detonation and normal shock wave parameters, (i. e., the "von Neumann spike" preceding the combustion zone) based on the idealized thermohydrodynamic theory of detonation, were computed for the same mixtures over a wider range of initial pressures, i. e., 1/2 to 1000 atmospheres. The theoretical and experimental values of detonation velocity and static pressure were critically compared. The experimental investigation was limited to the use of one detonation tube with no change in geometry or internal surface and to one particular method of ignition.

A high-pressure detonation test facility was used in the experimental investigation. The principal components used consisted of a



closed heavy-walled 1-1/2 inch I. D. , 16-foot long detonation tube, a gas handling system capable of instantaneously charging the detonation tube with precisely reproducible gases containing up to four components, an exploding wire ignition system, high precision 10 MC electronic chronographs in conjunction with ionization-probes to measure wave velocities, and piezoelectric quartz crystal pressure transducers in conjunction with a unique on-the-line-electronic compensation device to measure highly transient detonation pressures.

In the pages that follow will be found a discussion and evaluation of the pertinent literature information, a preliminary discussion leading to the plan of investigation; a presentation, discussion, interpretation and evaluation of the theoretical and experimental results and conclusions. Several appendices are included in which the postulated model of stable detonation wave is discussed, the basic equations required for the calculation of the detonation and shock parameters are derived, the procedure used to calculate the detonation and shock parameters by use of automatic computer techniques is presented, the experimental equipment, instrumentation, testing procedure and techniques used are described, and the calibration of the experimental equipment and instrumentation is discussed. Also, photographic results of the pressure measurements, and tables and graphs displaying the theoretical and calculated detonation velocities

and pressures and other detonation parameters obtained are included.

## II. LITERATURE REVIEW

### A. General:

A detailed historical review covering the classical and early studies pertaining to experimental and theoretical efforts on detonation will not be presented here. Reviews of this nature are available in books and treatises where comprehensive information on the phenomena together with complete chronologies are presented (31, 32, 67, 88, 106, 110, 125, 169, 154, 155, 196, 199, 216, 239, 320, 322). The main effort in this section will be concentrated on the review and evaluation of the recent research on steady-state fully-developed plane detonation waves, this work being intimately connected with the present investigation. However, because of their direct bearing to the overall understanding of the detonation phenomena, limited discussion is presented on the initiation of detonation waves by flames and the mechanism of propagation of such waves, on the structure of detonation waves, and on unstable and unsteady detonation waves. Spinning detonation, wave curvature, three-dimensional, spherical and oblique detonations, and detonation wave interactions are considered outside the scope of this investigation.

### B. Historical Background:

The identification and analysis of detonation as a supersonic combustion wave process, rather than a spontaneous explosion in

gaseous mixtures was first made by Berthelot and Vielle (19) and confirmed by Mallard and LeChatelier in 1881 (213). In addition, Mallard and LeChatelier, using a rotating drum camera, were the first to record the development of detonation from burning, the fully developed steady detonation wave, and certain ensuing oscillatory phenomena. The full explanation of these discoveries continue to occupy the energies of investigators in this field. Schuster (280) generally is given credit for recognizing the similarity between detonation waves and the impact waves of Riemann (265), Rankine (260) and Hugoniot (162). Chapman (46) and Jouguet (71, 171, 172, 173) about 1900 were the first to point out the significance of a plane reactive wave front and its relation to the shock front previously studied by Hugoniot (162).

#### C. The Rankine-Hugoniot Relationships (10, 31, 46, 67, 110, 125, 166, 171, 172, 199, 221, 281)

A brief presentation of the theory is given in Appendix I covering the important aspects of the Hugoniot representation of detonative combustion.

#### D. The Classical Chapman-Jouguet Detonation Wave Theory and Postulate

The thermohydrodynamic theory of ideal plane steady-state detonation waves was the result of the classical analysis of Chap-

man (46) and Jouguet (71, 171, 172, 173) as well as of Cussard (70, 71) and Becker (9, 10, 11, 12). Chapman and Jouguet, using experimental fact that the detonation process is quite stable and stationary, compared the state of the fresh gas with the state of the burned gas without considering the actual burning zone. The classical model of stable detonation postulated by Chapman and Jouguet considered the detonation wave to consist of a one-dimensional plane steady shock wave sustained by an exothermic chemical reaction, essentially a planar discontinuity in pressure, temperature and composition separating the initial and final mixtures with the chemical reactions occurring at infinitely rapid rates and reaching completion within the discontinuity (Kistiakowsky and co-workers (17, 176) and others later interpreted this state of complete reaction to be that of thermodynamic equilibrium in the Chapman-Jouguet plane).

Based on this model, and neglecting molecular diffusion, viscous and thermal losses, Chapman and Jouguet calculated the detonation velocity by using the relationships of mass, momentum and energy conservation leading to the Riemann and Rankine-Hugoniot relationships across the discontinuity, an equation of state, detonation product thermal data. In addition, since the conservation equations alone are insufficient for a precise specification of the end

state, they used a theoretical relationship specifying the exact point on the Hugoniot (See Point D, Fig. 1) which uniquely defines the detonation velocity. The choice of this point was based primarily on experimental evidence of the physical situation. This additional relationship, now identified as the classical Chapman-Jouguet hypothesis, stipulates that the velocity of the stable detonation wave is a singular solution of the conservation equations and is the minimum one compatible with the conservation conditions. The detonation velocity thus postulated was shown to be equivalent to the assumption that the detonation velocity,  $D$ , equals the sum of the particle velocity,  $u''$ , and the local Euler sound velocity,  $a''$ , in the detonation products:

$$D = u'' + a'' \quad (1)$$

or that the burned gases behind the detonation wave have a Mach number,  $M''$ , exactly equal to one relative to the wave front, i. e.,

$$M'' \equiv 1 \quad (2)$$

Alternately, the Chapman-Jouguet postulate can be expressed by the relationship

$$(dp''/dv'')_{C-J} = - \left[ \frac{p'' - p'}{(1/\rho') - (1/\rho'')} \right] \quad (3)$$

This relationship states that the Rayleigh line tangent to the Hugoniot curve (See Fig. 1, Curve ADF, at point D( $p''$ ,  $v''$ )) from the initial state, point A( $p'$ ,  $v'$ ) yields the pressure and specific volume

of the burned gas for the case of the steady detonation wave, and that at the Chapman-Jouguet point (  $p'', v''$  ) of the Hugoniot curve, the dynamic adiabatic and the ordinary ( static ) adiabatic curves coincide.

#### 1. Theoretical Justification of Chapman-Jouguet Hypothesis

The Chapman-Jouguet postulate has been discussed and theoretically justified on the basis of statistical mechanics and thermodynamics by Jouguet ( 172 ), Becker ( 10, 11 ), Scorah ( 281 ), von Neumann ( 5, 250, 304 ), Döring ( 88 ), Zeldovich ( 320, 321, 322 ) and others, as well as on the basis of hydrodynamics alone by Brinkley and Kirkwood ( 38 ). Some important aspects of their analysis will be covered in this study.

Jouguet ( 172 ) surmised that a rarefaction wave would necessarily form behind the detonation wave. This wave would overtake and weaken any strong detonation ( See Fig. 1, Curve ADF ) until the Chapman-Jouguet condition is reached. Therefore, the detonation wave could be stable only at points between G and C. Becker ( 10, 11 ) maintained that the burned gas would inevitably tend towards the state of the highest entropy possible due to statistical mechanical considerations. These considerations ruled out any points below D in Fig. 1. These conclusions lead to the result that the detonation wave, being mechanically unstable above D and thermodynamically improbable below C, will be stable only when traveling at a velocity corresponding to the point D.

Scorah (281) argued that the work content for the Chapman-Jouguet detonation state is a minimum. He inferred that this state corresponds to maximum degradation of energy. Brinkley and Kirkwood (38) presented proof of the stabilities of the Chapman-Jouguet state on the basis of straightforward hydrodynamics arguments alone by considering the interaction between wave propagation and expansion of the wave front. In their description of the detonation wave, they considered the reaction front to be infinitely thin; and the energy behind the wave was assumed to decrease continuously with time. They concluded that if a detonation wave is initiated with a peak pressure greater (or less) than that for the Chapman-Jouguet state, the pressure would decrease (or increase as the case may be) in the course of its propagation to that for the Chapman-Jouguet state and thereafter remain constant. Since all the properties of the detonation state are functions of the peak pressure only, these quantities will also remain constant after the pressure becomes constant. In particular, they concluded that the stable value of the detonation velocity is the constant value predicted by the Chapman-Jouguet hypothesis. Von Neumann (5, 250, 304), Döring (523) and Zeldovich (320, 322) independently justified the Chapman-Jouguet condition on the basis of stability arguments. They considered that the reaction actually does not take place in a sharp discontinuity front (Chapman-Jouguet theory) but rather in a zone of finite width. On the basis of their model, it was shown that with the shock wave preceding the reaction zone, the Mach number of



the detonated gases is necessarily less than unity and must approach unity under the influence of perturbations. This conforms with the Chapman-Jouguet postulate.

## 2. Experimental Confirmation of Chapman-Jouguet Theory

Although the theoretical arguments presented by the investigators previously cited were very convincing, in the opinion of this investigator and others they offer no complete vigorous proof of the Chapman-Jouguet postulate (199, 56, 108). The validity of the Chapman-Jouguet postulate is amply supported, however, by the reasonable agreement between calculated and observed detonation properties of many different gaseous mixtures obtained by many investigators (16, 17, 18, 47, 48, 103, 126, 127, 178, 180, 181, 182, 183, 184, 186, 210, 211, 225) under experimental conditions which make the one-dimensional approximation a good one; i. e., detonations in quiescent gaseous mixtures contained in smooth channels of unvarying and sufficiently large cross-section. (See Section II-I-1 for details of previous detonation measurements and calculations). The applicability of the thermohydrodynamic theory to gaseous detonations, as well as to condensed explosives, (56) when considered from the macroscopic viewpoint, i. e., not considering the details of the reaction wave structure, is now widely accepted as an empirical fact for the theoretical prediction of steady detonation properties.

For all the mixtures considered, over a relatively wide range of compositions, initial temperatures, and pressures, these investigators found excellent agreement between experimentally determined detonation velocities and velocities calculated assuming thermodynamic equilibrium rather than complete reaction in the Chapman-Jouguet state. Most of the investigators inferred, therefore, that for these mixtures thermodynamic equilibrium was attained in the Chapman-Jouguet plane and that the Chapman-Jouguet theory applied rigorously to these particular mixtures.

Berets, Greene and Kistiakowsky (17) had some reservations, however. They concluded that the Chapman-Jouguet theory applies rigorously to these mixtures, but only in the sense that the detonation velocity may be set equal to the sum of the acoustic and mass velocities of the equilibrium mixture, making it the lowest velocity consistent with the Rankine-Hugoniot conditions for the mixtures. They submit that agreement of calculated and experimental velocities is not conclusive proof that thermal or chemical equilibrium are accurately established in the detonation wave. They inferred that the calculated velocity is not very sensitive to the precise equilibrium assumed, and they suggested that the excellent agreement which is usually observed between theoretical and experimental velocities may be due to the stabilizing or buffering action on the detona-

tion velocity of the largely dissociated reaction systems, in which exothermic and endothermic reactions involving both mole increment and decrement are preceding simultaneously. They maintained that seemingly perfect agreement between experimental velocities and theoretical velocities can be obtained without the theory being accurate in detail. To test the theory, they indicate it would be necessary to measure not only the velocities but the temperature and densities ( or pressures) in the Chapman-Jouguet plane. Berets', et. al. ( 17) interpretation was rejected later by Kistiakowsky and Zinman, ( 186) who maintain that agreement between experiment and equilibrium calculations is sufficient proof of the attainment of thermodynamic equilibrium in the Chapman-Jouguet plane.

Ubbelohde and Copp ( 196), Cook ( 55), and others, and this investigator, agree with Berets, et. al. ( 17) pertaining to the insensitivity of the calculated detonation velocity to the precise equilibria assumed. They infer that more refined methods of analysis, including determination of additional detonation parameters simultaneously with velocity in the Chapman-Jouguet plane, will permit more realistic determination of the attainment of chemical and thermal equilibrium in a detonation wave. Also, these will permit better assessment of the validity of the Chapman-Jouguet theory.

Peek and Thrap (248, 249) based on their precise investigations with cyanogen-oxygen-nitrogen mixtures, concluded that it is necessary to consider the kinetic details of the detonation reaction, stipulated by Kirkwood and Wood (174) in their postulated theory of the detailed structure of the detonation wave, in order to show that the Chapman-Jouguet state is the state of thermodynamic equilibrium. They argue that since experimental data on reaction kinetics at detonation temperatures are not available, it is not possible at the present time to demonstrate conclusively that thermodynamic equilibrium is attained in the mixtures investigated. They question somewhat the comparison of experimental and theoretical results to demonstrate the validity of the Chapman-Jouguet theory. This investigator agrees with the above conclusions of Berets, et. al. (17), Ubbelohde and Copp (169), Cook (55) and Peek and Thrap (248, 249). In addition, this investigator feels it is necessary to have precise knowledge of the energy dissipation due to transport phenomena, as well as precise values of the real gas thermodynamic properties of the initial and product gas species. It is pointed out further that the majority of the tests discussed above were conducted at or near ambient initial pressures and temperatures. Very little work has been done at elevated initial pressures.

### 3. Deviations from Chapman-Jouguet Theory

Deviations from the detonation values predicted by the classical

Chapman-Jouguet theory, have been encountered. This is not too surprising, though, since, among other things, the theory predicts a detonation velocity which is independent of the size or shape of the containing vessel, i. e., no energy losses due to dissipation, such as viscosity or heat conduction (wall effects). Also, the theory assumes that complete chemical and thermal equilibrium is achieved by the detonation products instantaneously in the wave discontinuity.

Determinations of the completeness of thermal and chemical equilibrium attained in the Chapman-Jouguet state of steady-state detonation waves and estimations of the influence of viscous drag and/or heat transfer to the wall (wall effects) have been carried out experimentally and theoretically. Pertinent comments pertaining to the results obtained and conclusions drawn by a number of these investigators will be summarized in this review.

#### (1) Non-Attainment of Complete Thermal and Chemical Equilibrium

Kirkwood and Wood (174) have recently shown theoretically that thermodynamic equilibrium at the Chapman-Jouguet point is not an essential requirement in the generalized theory. Deviations from complete equilibrium, as well as viscous drag and/or heat transfer, are expected to give rise to differences between experimental detonation wave parameters and those computed assuming equilibrium and no losses. Under these conditions Zeldovich (320, 322) and Kistiakowsky (17) infer that the actual Chapman-Jouguet plane should be defined

as the final state of the gas in the steady or constant region that proceeds the expanding portion of the wave. This state will be influenced, of course, by losses that have occurred before the gas has reached this point. Thus, if the rate of chemical energy release within the reaction zone is lowered, for example by cooling of the reacting gases at the walls of the confining vessel (rarefaction wave) (17), then the rate of production of useful energy may drop below the level required for propagation of the ideal Chapman-Jouguet wave. In this case the detonation wave velocity generally will be less than the ideal value calculated on the basis of complete equilibrium because some of the energy is not utilized. The Chapman-Jouguet condition, ( $D = u'' + a''$ ) now will hold for the plane in which the energy required to propagate the wave; i. e., the useful energy, is just balanced by its losses. The rest of the energy obtained from the spontaneous reaction, Kistiakowsky (17) says, occurs in the rarefaction wave and has no effect on the detonation wave propagation. In this same vein, Zeldovich (320, 322) pointed out that an endothermic reaction lagging behind the exothermic processes responsible for the detonation will not be included in the Chapman-Jouguet state and will occur in the rarefaction wave where it has no effect on the detonation wave parameters. Kistiakowsky and co-workers (47, 178, 183, 186) and Basu (8, 121), from their observations of "double waves" in acetylene-oxygen and benzene-oxygen mixtures offer additional experimental evidence to support the

postulates of Zeldovich (320, 322) and Kirkwood and Wood (174)

As indicated previously, Lewis and Friauf (195), in their experiments with hydrogen-oxygen-diluent (nitrogen, helium, argon) mixtures, found excellent agreement between theoretically calculated and experimental detonation velocities, where the hydrogen and oxygen concentrations were not far from stoichiometric and where the diluent concentration was relatively low. However, significant differences were found between calculated and observed velocities at the extremes of composition range. They suggested that the velocity deficit, i. e., experimental velocities lower than Chapman-Jouguet calculated velocities, under these conditions, was due to incomplete chemical reaction occurring in the detonation wave reaction zone which would reduce the wave velocity below its theoretical value.

Berets, Greene and Kistiakowsky (17) conducted tests with similar mixtures in tubes of 1.2 and 10 cm. diameter, respectively. They too found good agreement between experimental and theoretical values of detonation velocity only at conditions near stoichiometric. They also observed a difference in detonation velocity in the different diameter tubes, the velocity being less in smaller than in the larger tube. Like Lewis and Friauf (195) they found significant differences in calculated and observed velocities at the extremes of the composition

range: lower velocities in mixtures with excess hydrogen and higher velocities in mixtures with excess oxygen. Here also the difference of velocities measured in wide and narrow pipes was larger. (During the course of later investigations Kistiakowsky and Zinman (186) reported that the high velocities observed in the mixtures with excess oxygen were due entirely to overdriving of the mixture by the shock initiator.) Kistiakowsky and Zinman concluded that the observed deviations from theory were only partially explainable by losses of energy to the walls of the tube (cooling and friction) through the formation of a rarefaction wave spreading into the reaction zone. These energy losses would cause a lowering of the temperature which would, in turn, reduce the rate of chemical reaction and thereby cause a lowering of the detonation velocity. They gave evidence to show that in addition to the heat losses, non-attainment of thermal and chemical equilibrium in the Chapman-Jouguet plane contributed to these deviations. The conclusions of Beret's et. al. (17) have been supported by other investigators including Kistiakowsky and Kydd (182) and Cher and Kistiakowsky (47), who measured velocities as well as reaction zone densities using x-ray techniques; Kistiakowsky and Tabbutt (184), who studied the progress of the chemical reaction in the detonation wave by absorption spectrographic means; Edwards, Williams and Breeze (103) who measured velocities as well as detonative wave pressures; and Gordon and Mooradian (134).



#### 4. Speed of Sound in a Reacting Gaseous Mixture

There has been considerable concern recently about the uniqueness of the definition of the Chapman-Jouguet point. This involves the question of which velocity of sound should be used in the theoretical calculation of detonation wave properties in a reacting gaseous medium. To date, this question has not been satisfactorily resolved. Von Neumann, in the postulation of his detonation (NDZ) theory (120, 304), maintains that the flow velocity, when equilibrium is reached at the upper Chapman-Jouguet point, is equal to the local "equilibrium" sound speed, i. e., the wave of minimum value of detonation velocity. Zeldovich (321), Brinkley and Richardson (39), and Kirkwood and Wood (174) disagreed with von Neumann and pointed out that since, in a chemically reactive wave, pressure is a function not only of density and entropy, but also of chemical composition, the speed of sound for a reacting mixture should be defined as the "frozen" sound speed, i. e., the sound speed in a chemically "frozen" equilibrium mixture. In particular, Brinkley and Richardson (39) maintain that if an expansion wave is not to overtake a detonation, the Chapman-Jouguet condition would require that the flow velocity with respect to the wave front equal the "frozen" sound speed when equilibrium is reached. Kirkwood and Wood (174) considered the kinetic equations defining the time rate of change of chemical composition together with the conservation equations in

their analysis and arrived at the same conclusion as Brinkley and Richardson, with the exception of the possibility of "pathological" detonations first suggested by von Neuman (110, 304, 238). The pathological cases may occur if either there is a volume decrement or an endothermic reaction under local conditions. No example of a pathological detonation has been established (55, 110). In subsequent work, Wood and Kirkwood (312, 313) pointed out that the "frozen" Chapman-Jouguet sonic point lies below the equilibrium Chapman-Jouguet point on the equilibrium Hugoniot. They concluded further that for cases involving a single reversible reaction, the existence of the "frozen" Chapman-Jouguet point is uncertain. For general reaction schemes (313), they stated that there may be no solution of the conservation and kinetic equations which passes through the "frozen" Chapman-Jouguet point. They also found that the proper Chapman-Jouguet condition is uncertain, and that the reaction zone can be steady only in an asymptotic sense. The several solutions involving reversible reactions which have been computed support this contention. Duff (89, 95) found that the final state is on the upper branch of the equilibrium Hugoniot; and Linder, Curtiss and Hirschfelder (206) found that the final state is at the "equilibrium" Chapman-Jouguet point. Wood and Salzburg (314), using the method of non-linear mechanics, also concluded that the "frozen" Chapman-Jouguet condition is structurally unstable. Cross (105, 142) and

Edse (52, 101) point out that the calculated detonation velocity is quite similar whether determined on the basis of the "frozen" or "equilibrium" speed of sound. However, the pressure, temperature, density and composition are significantly different. The "frozen" speed of sound is for most Chapman-Jouguet stoichiometric fuel-air mixtures (105, 142) larger than the "equilibrium" speed of sound, and their ratio is of the order of 0.96. Edse (102) and Edse and S. T. Chu (52) presented methods for calculating the specific heat ratio, speed of sound and Mach number in both chemically reactive and non-reactive gas mixtures. Edse (102) includes the determination of shock as well as detonation parameters.

Penner (250) pointed out that the physical process of the detonation wave, utilized by Kirkwood and Wood (174) and some of the other investigators cited above, in their analyses involves the hypotheses that relaxation effects (e. g., adjustments of internal degrees of freedom) occur instantaneously whereas the chemical reactions take place more slowly. This oversimplification allows the detonation phenomenon to be treated by a single perturbation treatment, as was done by B. T. Chu (51). Penner maintains that to date a really satisfactory analysis of the nature of steady-state detonation processes allowing for arbitrary relaxation times of internal degrees of freedom and chemical reaction rates has not been given on the basis of a model

neglecting viscous effects, diffusion and heat conduction. He states further that the possibility that "steady" detonations do not exist cannot be dismissed with certainty.

Experimentally, the question concerning the product gas sound speed has not been resolved. Peck and Thrapp (248, 249) using precise velocity measurements and calculations failed to distinguish convincingly between the "frozen" and "equilibrium" Chapman-Jouguet hypothesis. Duff, Knight and Rink (95) point out that the "frozen" and "equilibrium" Chapman-Jouguet densities differ by more than 10%, and their accurate x-ray absorption measurements give densities very close to the "frozen" Chapman-Jouguet value. Fay and Opel (118, 122) question the validity of Duff's interpretation of his density data based totally on the Kirkwood-Wood theory (174). Fay states that the state of the gas a short distance behind the front does not correspond to the value calculated from one-dimensional flow relations according to either the "frozen" or "equilibrium" sound speed hypothesis. Fay emphasizes that the flow field is strongly affected by two-dimensional effects engendered by the viscous boundary layer wall friction and heat transfer, and that these effects must be considered in the interpretation of experimentally determined detonation properties. Duff and Knight (94) and Wood and Kirkwood (313), citing conflicting experimental evidence and

recent theoretical developments, respectively, are not convinced that Fay's interpretation of Duff, Knight and Rink's observations is correct. In particular, Wood and Kirkwood acknowledge that the two-dimensional effects observed by Fay and Opel (122) may be important in finite tubes, but that the flow acceleration apparently observed by Fay and Opel might be related to the fact that even for a normal detonation the reactions are incomplete at the Chapman-Jouguet point in a tube of finite diameter. Obviously, a need for additional research in this area is indicated. Gordon and Mooradian (134) and Edse (101) state that for dilute mixtures where there is little dissociation, choice of either the "frozen" or "equilibrium" sound speed makes very little difference.

#### E. Recent Theories and Models of Detonation Wave Structure

The classical theory of Chapman and Jouguet, as indicated previously, can predict the gross detonation properties in a great number of cases with considerable accuracy solely from thermodynamic consideration without consideration of chemical kinetics or transport phenomena. However, the classical theory assumes a detonation reaction of infinite rate, a reaction zone of zero thickness, and complete chemical reaction with attainment of peak pressure. Thus, it provides no information pertaining to the internal structure of the detonation wave; e. g., reaction zone thickness, shape, stability, etc.

Actually, the reaction rate is finite; and hence there must be a reaction zone of finite width with attendant temperature and pressure gradients. In the case of detonations in very lean gaseous mixtures or at low initial pressures, the wave has been found to be quite extended by Bone, Fraser, and Wheeler (29, 30), Morrison, Nicholls, and Cullen (224, 232), Pusch (258), Opel (120, 122), Schmidt, Steinicke and Neubert (279), Grier, Cooper and Gibson (138), and Martin and White (218, 219). For the richer mixtures, the wave appears to have a relatively clean discontinuity. For the leaner mixtures the reactions extend over a much greater time, and the initial shock with some combustion is trailed by oblique shock waves as well as by residual combustion. No clear explanation of these effects have been given to date. Fay (119, 120, 122) and Zeldovich (320, 321, 322) and others maintain that the wall boundary layers play an important role in this phenomena, leading to two-dimensional effects. Hirschfelder, Curtiss, Linder and Barnett (72, 73, 153, 206), Adamson (2) and Cook (57, 65) infer that the structure of the wave under certain conditions is appreciably influenced by heat conduction and viscosity; i. e., transport properties. It is quite possible that these effects contribute to observed detonation wave structure under particular conditions.

A number of recent theories have been postulated in attempts to

analyze the detonation wave structure, and especially the region between the Chapman-Jouguet plane and the detonation front, namely the "effective" reaction zone. With but few exceptions, the theory of the detonation wave structure has been concerned with the postulation of relatively simple models in which only the important mechanisms are retained; i. e., steady, plane (i. e., one-dimensional) waves with no transport effects considered. This was done to avoid a simultaneous solution of the conservation equations including transport phenomena and the equation of state. Also due to the complexities involved in a complete description of the chemical kinetics which hold in even the simpler reactions, only the simplest reaction mechanisms have been employed to date.

1. Von Neumann-Döring-Zeldovich (NDZ) Model of the Structure of the One-Dimensional Detonation Wave

Among the most important of the modern theories dealing with the detonation wave structure is that independently postulated by von Neumann (304) Döring (87, 88) and Zeldovich (320, 321, 322). Their particular model of a chemical detonation wave is based on the hypothesis that reaction velocities in the unburned or partially burned gases are too small to maintain a steady detonation wave without pre-compression by a shock wave, and also that the propagation time for a shock wave is short compared with the time required for chemical reactions to occur. Following directly the hypothesis of Chapman and Jouguet (46, 171), they assumed a simplified (NDZ) model in

which the detonation was considered to be a composite wave consisting of a non-reactive plane shock wave followed immediately by a deflagration. They postulated that the shock wave, propagating into the unburned or neutral mixture, compresses and heats the unburned gas thus initiating chemical reaction. The shock wave of a few mean paths thickness is followed by a steady-state reaction zone where rapid chemical reactions occur, and in which the temperature rises and the density falls as the combustion process proceeds towards chemical equilibrium. The reaction zone is terminated at the classical Chapman-Jouguet condition on the equilibrium Hugoniot (See Fig. 1, point D). Here the local flow velocity plus the equilibrium sound speed equals the detonation velocity, and complete thermodynamic equilibrium exists. Following the Chapman-Jouguet plane is an unsteady regime of the isentropic rarefaction or Taylor wave (292, 293) followed finally by quiescent gas. The detonation velocity is determined solely by the equilibrium conditions and is not affected by the rate of chemical reaction. Only the width of the reaction zone depends on the reaction velocity, being wider for lower reaction rates. Thus the Chapman-Jouguet thermodynamic equations alone, without consideration of chemical reaction rate, can be used to calculate the detonation velocity and other detonation parameters when external energy losses are negligible.

The approach used by von Neumann, Döring and Zeldovich was



concerned with the Rankine-Hugoniot relationships for the conservation of mass, momentum and energy. The effects of transport properties were neglected by all of them, as a first order approximation, in the description of the detonation wave structure. No reaction kinetics were employed, the extent of reaction or condition in the reaction zone being characterized by a parameter "N", corresponding to different degrees of completion of reaction or fraction of total available energy addition. "N" varies from zero, for the non-reactive plane shock wave at the cold boundary, to unity, for the completely reacted mixture at thermodynamic equilibrium at the hot boundary. In the absence of dissipation effects, "N" represents also the mass fraction and the mass rate fraction of products passing through a section of the reaction zone.

The detonation process as proposed by von Neumann, Döring and Zeldovich can be visualized better by making use of the Hugoniot diagram. The conditions in the reaction zone can be obtained by construction of a family of Hugoniot curves in the  $(p, p^{-1})$  plane corresponding to different values of "N". In Figure 1, the Hugoniot curves are drawn for the non-reactive shock wave ( $N=0$ , Curve A'C') and for the completely burned gas at equilibrium Hugoniot - Curve ADF). If the postulate is made that all end states for detonation lie along the upper tangent (Chapman-Jouguet point) to the Hugoniot curve for the completely burned gas, then all the possible states of gas must

lie on the Rayleigh line A'D'G' (Figure 1). Initiation of the chemical reaction in the front of the reaction zone must be brought about by a discontinuous jump from point A', corresponding to conditions in front of the shock discontinuity, to the point G' for conditions immediately behind the shock front. Chemical reactions cannot be initiated at the shock front if the "N" characteristics of the reaction zone corresponds to point A', since this is the state of the initial mixture where no chemical reaction occurs. This leads to the conclusion that the state of a mass element changes abruptly from A' to the G'. Then following the compression, the chemical reaction proceeds so that "N" goes from 0 to 1 along the Rayleigh line, A'D'G', until the final state is reached at the point of tangency D, on the equilibrium ( $N=1$ ) Hugoniot curve, or at the classical Chapman-Jouguet condition. The particular states of the gas in the reaction zone or wave interior during the process are identified by the intersection of the Rayleigh line with one of the "N" family of Hugoniot curves for the reacting mixture. The front portion of the NDZ detonation, since it consists of a shock, produces very rapid increases ("von Neumann spikes") in  $p$ ,  $\rho$ , and  $T$  over spatial distances corresponding to the thickness of shock fronts (i. e., a few mean paths). The pressure and density then decrease slowly behind the shock front, with the pressure falling roughly to one half its maximum value. The temperature increases as the reaction goes to completion and may show one (or more) relative maxima before reaching a value which is roughly double the tem-

perature immediately behind the shock front (154, 194, 224, 252).

Von Karman (303) considered the same model as von Neumann, Döring and Zeldovich in noting the essential differences between a detonation and a deflagration wave. In his presentation he also established the form of the parameter to be used in deciding upon the relative importance of the transport properties. He defined a quantity " $\alpha$ " as the ratio of the characteristic thermodynamic time to the characteristic chemical time. Depending on the magnitude of " $\alpha$ ", it is either important (as in deflagration,  $\alpha \gg 1$ ) or it is not important (as in detonation,  $\alpha \ll 1$ ) to consider the detailed structure of the reaction front in prediction of observable propagation velocities.

Kistiakowsky (176), Lewis and von Elbe (203) Finklestein and Gamow (123), and Mallory and Jacobs (215) propose a modification to the original NDZ model. They maintain that a more correct and realistic model of the detonation wave should include an "induction period" between the shock front and the flame. In other words they claim that the reaction does not begin at the initial shock front but rather that it is preceded by a steady induction zone where little or no reaction occurs. In this model the fraction of explosive reacted initially changes very little, and the pressure and density profiles

are very flat for some distance behind the shock front, i. e., in the induction zone. They then drop sharply as the reaction goes to completion at a high rate. It is this modified NDZ version of the detonation wave that is postulated in the present investigation. It is believed that it most nearly describes the real situation under normal initial conditions and in most mixtures. Also, it should apply even better at the higher initial pressure conditions. (See Appendix I.)

Many attempts have been made to observe the predicted "spike" (i. e., non-reactive plane shock wave immediately preceding the reaction zone) of the von Neumann-Döring-Zeldovich theory and to measure the width of the reaction zone. To date there is no unambiguous evidence which has proven or disproven conclusively the existence of the sharp "spike" of the magnitude predicted by the theory in gaseous explosive. Kistiakowsky and co-workers (48, 182, 186) measured the variation of density with position within the reaction zone of a gaseous Chapman-Jouguet detonation wave by x-ray absorption photometry. The gases were hydrogen-oxygen, carbon monoxide-oxygen, methane-oxygen, and acetylene-oxygen mixed with sufficient added krypton or xenon (10-15 mm.) to give adequate x-ray absorption. The reaction zone could not be detected at all in acetylene-oxygen mixtures at one atmosphere or in stoichiometric hydrogen-oxygen mixtures above 95 mm. initial pressure, using equipment which had a time resolution of less than 0.5 micro-

seconds. Below 95 mm, Kistiakowsky, et.al., claimed, however, to have observed the reaction zone of several millimeters in thickness; e.g., at 0.1 atmosphere, the reaction zone had a duration of 3 microseconds and at 0.025 atmosphere, a duration of 20 microseconds. Their observations indicated that the reaction begins almost immediately upon arrival of the shock front. No induction period was observed of high constant density, at least of dimension comparable to the reaction zone width itself. Instead there was a very rapid rise in density at the wave front followed by a gradual decrease through the zone, as expected, to a constant value. The peak density at the wave front was only two-thirds of the full shock value expected from the von Neumann model. The constant value at the end of the reaction zone compared well with the calculated Chapman-Jouguet value based on equilibrium calculations (within 10 per cent experimental accuracy); i.e., good agreement with the Chapman-Jouguet theory of detonation. They concluded that the observed shape of the density profile showed qualitative agreement with the NDZ theory; however, the observed density peaks were substantially lower and the initial chemical reaction rates were faster than expected. They indicated that the lower observed peak density might be due to the lack of equilibrium between translational and internal degrees of freedom in the shocked gas lasting only long enough for a substantial progress of the chemical reactions to take place.

Kistiakowsky, et. al. , also found that the finite width of the reaction zone varied as the inverse square of the initial pressure of the detonative gases. They inferred that their inability to observe the reaction zone and spike at initial pressures of 1 atmosphere down to 95 mm. was due primarily to the fact that the reaction time was too short; e. g. , in the order of 0. 1 microsecond at 1 atmosphere considering a wave thickness of less than 1 mm. This would require a rise time of less than 0. 1 microsecond ( at atmospheric pressure) which was too small to be resolved with their apparatus. Chesick and Kistiakowsky ( 48) found that observed wave front density at the lowest test pressure ( 24 mm. ) was higher than that at the higher test pressures, undoubtedly due to the increased reaction zone width permitting more time for observation. They also found that the addition of appreciable quantities of inert gas, e. g. , argon at 309 mm, shortened the reaction zone to such an extent that it was also no longer observed with the resolving power of their instrumentation.

Duff ( 89) was able to rationalize exceedingly well the measurements of Kistiakowsky and Kydd ( 182) for a detonation wave structure extending over a few millimeters thickness, on the basis of an NDZ model with quite realistic kinetics. Duff calculated the reaction profile of the stoichiometric hydrogen-oxygen-xenon mixture (  $2\text{H}_2 + \text{O}_2 + \text{Xe}$  ) one of the mixtures studied by Kistiakowsky and Kydd ( 182) . He used

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the density values of Kistiakowsky and Kydd (182), incorporated a correction reflecting the lack of vibrational excitation between the shock and combustion zone, and assumed that a reasonable amount of wave tilt existed. Duff found quite reasonable agreement between his calculated results and Kistiakowsky and Kydd's experimental results. No measurable induction zone under normal detonation conditions was indicated.

Gordon and co-workers, (132, 133, 134) using piezoelectric pressure transducers attempted to measure the pressure within the detonation reaction zones of hydrogen-oxygen and hydrogen-oxygen-argon mixtures over an initial pressure range of 0.5 to 2 atmospheres. They inferred from their pressure traces that they had observed the von Neuman "spike" in argon diluted mixtures. (This investigator believes there is some question as to the validity of these conclusions in view of the assumptions made in the analysis of their data.) The von Neuman "spike" was not observed in any of the pure hydrogen-oxygen mixtures due to the fact that the reaction time was too small to be resolvable with their pressure-gage equipment. They did obtain an indication of a falling pressure in the combustion zone and found that the Chapman-Jouguet pressure was achieved almost immediately behind the wave front. The Chapman-Jouguet pressure observed was about 20% lower than the calculated value. This discrepancy they attributed to heat losses. They concluded that the detonation in the



hydrogen-oxygen-argon mixtures follows the von Neuman model. Gordon ( 132, 134 ), Kistiakowsky and Kydd ( 182 ), and Patterson ( 244 ), found reasonable agreement with the one-dimensional rarefaction wave theory as proposed by Doring and Burkhardt ( 87, 88 ), Pfriem ( 254 ) and Taylor ( 292 ), i. e. , reasonable agreement between measured and calculated pressure, velocity and density profiles in the unsteady rarefaction wave which follows the steady detonation wave ( Chapman-Jouguet plane ).

Edwards, Williams and Breeze ( 103 ) attempted to measure the pressures in the reaction zones of hydrogen-oxygen mixtures at 1 atmosphere initial pressure, utilizing pressure bar techniques. Due to the limited time response of the pressure measuring system, they did not expect to obtain an exact response to the peak pressure; i. e. , the von Neumann "spike. " They did observe, however, a rounded-off sharp pressure peak which they attributed to the partial response of the pressure gage to the von Neumann "spike" or normal shock front. They also found an indication of the falling pressure in the combustion zone and that the Chapman-Jouguet pressure was achieved almost immediately behind the detonation front. ( This investigator believes that the pressure peaks observed by Breeze, et. al. ( 103 ) may not have been truly indicative of the events occurring in the detonation wave. Rather the pressure peaks observed may have been due to the characteristics of the pressure-indicating device used. )

## 2. Cook "Heat Pulse" Model

Cook (57, 65) maintains that the fundamental NDZ model should be modified to include appreciable heat conduction in the reaction zone, i. e., an extremely intimate compiling between the reaction zone and the shock wave (heat-pulse theory). He indicated that with appreciable heat conduction the necessity disappears for the "spike," or at least a spike of the magnitude stipulated by the von Neumann-Döring-Zeldovich theory. He indicated further that if the heat conduction is of sufficient magnitude the necessity for an induction zone also could be removed. In his model of detonation, the pressure is nearly constant at the Chapman-Jouguet pressure; i. e., no pressure spike or induction zone.

Cook contended that the heat of combustion is trapped in the reaction zone through thermal conduction and carried along as a "heat pulse." The effect of this is to raise each Hugoniot curve (see Fig. 1) of  $N = N_i$  by an amount depending on the magnitude of the heat pulse added by heat conduction to the  $N_i$  region in the reaction zone. The result is a family of Hugoniot curves, all of which intersect the Rayleigh line at the same point; the Rayleigh line is tangent to this point (the Chapman-Jouguet condition) through the initial condition point (Point A, Figure 1). The reaction path of the Cook "heat pulse" model on the  $(p, p')$  plane (see Figure 1) starts at the initial condition,

A, on the tangent Rayleigh line and continues to D. The velocity of the burned gas always is decreasingly supersonic until the Chapman-Jouguet point for the gas is reached (Point D, Figure 1).

Cook (58, 65) analyzed the experimental data published by Kistiakowsky and co-workers and maintains that they agree better with his modified NDZ "heat pulse" theory of detonation than with the fundamental NDZ theory of detonation. He also presented experimental evidence (64, 65) in support of his model of detonation. The evidence is not considered by this investigator and others (111, 252) as conclusive proof of the Cook "heat pulse" model.

### 3. Hirschfelder - Curtiss Model of Detailed Structure of the One-Dimensional Detonation Wave

The von Neumann-Doring-Zeldovich model of a detonation wave is based on the assumption that viscous dissipation, heat conduction and diffusion effects may be neglected, in the first approximation, in the description of the detonation wave structure. There is considerable disagreement regarding the importance of this assumption, i. e., the importance of transport effects in detonation phenomena. Hirschfelder and co-workers (72, 73, 153, 206) state it would be impossible to have a shock wave without viscosity or heat conduction, as there would be no mechanism for changing the entropy of the gas. Kistiakowsky (176) maintains that transport properties do not

affect appreciably the behavior of a detonation wave. Zeldovich ( 320, 321, 322) also argues that such effects are negligible unless some chemical reaction is complete within a few kinetic mean free paths. This he rejects as chemically implausible. Brinkley and Richardson ( 39) hold the same views as Zeldovich.

Hirschfelder and co-workers ( 72, 73, 153, 206) maintain that in real detonations the von Neumann "spike" is rounded off by the action of these transport effects under certain conditions. Recently Hirschfelder and co-workers have vigorously attacked the problem of ascertaining the detailed structure of the steady-state plane gaseous detonation wave. They considered the most general model of detonation; i. e., inclusion of viscous dissipation, heat conduction and diffusion effects, as well as chemical kinetics. No shock was postulated. Instead Hirschfelder, et. al. solved numerically the differential equations of conservation of mass, momentum and energy in the wave interior under some simplifying chemical kinetic assumptions. Effects of viscosity, diffusion and thermal conductivity were included. Hirschfelder, et. al., obtained composition, pressure and temperature as a function of distance in the wave interior for various cases. It is important to realize that when viscous dissipation is included, Equation AII-9, Appendix II ( the Rayleigh line) no longer holds. Therefore the reaction paths in the Rankine-Hugoni-

ot plane no longer follow the Rayleigh line; i. e. , the upper Chapman-Jouguet point may be reached along a non-linear path. The exact path for passage from the initial state to end state ( Chapman-Jouguet point) is left open; and as Hirschfelder et. al. indicated, several alternate solutions are possible. As one of the solutions, i. e. , the zeroth order solution to the more general problem where coupling between shock and reaction portions of the detonation are small or transport effects are negligible, Hirschfelder, et. al. , obtained solutions quite similar to the fundamental NDZ model. In other examples studied, Hirschfelder found that there was strong coupling between the reaction zone and the shock zone, i. e. ; sufficiently fast reaction rate, so that the solutions never exhibited the height of the von Neumann "spike." In fact, they approach the Cook "heat pulse" model described previously ( See Section IIE-2). They stated that the structure of any actual detonation lies between the NDZ "spike" model and the Cook "heat pulse" model.

It should be pointed out that Hirschfelder, et. al. indicate that the width of the reaction zone, based on their final solution for the wave profile in space, is on the order of a few kinetic mean free paths. This has been indeed pointed out by the authors as the main flaw in their analysis. They suggested consequently that the ordinary concepts of local temperature and reaction rates evidently break

down and that the rate may be determined by some unusual kind of relaxation process. This latter argument of Hirschfelder, et. al., in support of their analysis based on their contention that transport properties are important in determination of the wave structure, lacks strength. On the other hand, in support of the viewpoint of Zeldovich, Döring, von Neumann, Kistiakowsky and Brinkley and Richardson, who contend that transport effects are negligible, all measurements to date have shown reaction zones of the order of  $10^4$  mean free paths in thickness (39, 73, 120, 218, 219) Adamson (2) and Wood (311) attacked the same problem solved numerically by Hirschfelder, but they used instead an approximate analytical solution; i. e., a perturbation solution. The model of detonation chosen was that of a shock followed by reaction, so that in the zeroth order it is essentially the same as the von Neumann model.

Gross (140, 141, 142) indicated that his experimental observations of standing detonations in his wind tunnel installation give strong support to Hirschfelder's contention that transport properties within a detonation wave are important, since conditions behind a shock wave at the stagnation temperature in his experiments were far too low to produce thermal ignition. Nicholls (141, 229, 230, 231, 232), on the basis of his observations on standing detonations in a wind tunnel set-up, disagrees with Gross and contends that the influence of transport properties is very small.

#### 4. Two Dimensional Gaseous Detonations and Wall Effects

As stated previously, the classical Chapman-Jouguet theory or the NDZ theory does not allow for energy losses to the walls, or the effects of fluid viscosity and surface friction at the boundary. Even though it seems reasonable that these effects might reduce the wave velocity below its ideal value, early experiments by Campbell (43) failed to reveal any effect of tube size on detonation velocity. However, Shchelkin (81, 282, 283) showed that a wire spiral laid along the tube wall to produce surface coarseness, could appreciably reduce the wave velocity under particular conditions to 50 - 60 percent of the velocities expected if surface roughness had not been present. Zeldovich (320, 321, 322) found it necessary to abandon the limiting restrictions of the classical one-dimensional Chapman-Jouguet theory in order to explain this phenomena; i. e., the one-dimensional theory breaks down in coarse-wall tubes. He proposed a quasi-one-dimensional theory in which frictional drag and heat losses were considered to be uniformly distributed throughout planes normal to the tube axes, and he showed that the reduction in wave velocity should be proportional to the reaction zone thickness and inversely proportional to the tube diameter. He also noted, as indicated previously, that the Chapman-Jouguet conditions should be modified under such circumstances (See IID-3 of this section), the flow becoming sonic not at chemical equilibrium, but when the rate of chemical reaction balances the frictional force and heat loss to give a non-singular

behavior at the sonic line. Döring ( 87, 88 ) presented a qualitative interpretation of the effects of finite tube diameter similar to that of Zeldovich. The correctness of Zeldovich's qualitative analysis is supported by the work of numerous investigators. Kistiakowsky and co-workers, ( 17, 178, 179, 180 ) as previously mentioned, measured detonation velocities in tubes of 10 to 1.25 cm. diameter; Guenoche and Manson ( 143 ) measured detonation velocities in tubes varying from 1.16 cm to 1.16 mm diameter. These and numerous other investigators found that the detonation velocity is less in small- than in large-diameter tubes. A related phenomena is present in the detonation of unconfined solid explosives, where the detonation velocity varies with the charge diameter ( 179 ). Kistiakowsky, et. al. ( 17, 178, 179, 180 ) attributed a portion of this "velocity deficit" to energy losses to the tube walls. They found, that to a good approximation a plot of detonation velocity vs. reciprocal tube diameter was a straight line whose intercept agreed closely with the Chapman-Jouguet theory. Consequently, they stated that the excess of velocity for an infinite tube diameter over that for a finite tube diameter was inversely proportional to the tube diameter. On this basis, they concluded that measured velocities in finite tubes could be extrapolated to infinite tube diameter for comparison with the Chapman-Jouguet plane wave theory. In order of magnitude, the velocity deficit was about 1 percent of the propagation velocity in a tube of 1-cm. diameter for several common mixtures. Kistiakowsky,



Knight and Malin (179) also found that the wall effect was independent of gas composition.

Mooradian and Gordon (132, 134, 223) measured detonation velocities of hydrogen-oxygen-diluent (helium, argon, nitrogen) mixtures in a 3/4 inch diameter tube at initial pressures of 1/4 to 3 atmospheres. They found a related effect to that observed by Kistiakowsky, et. al., and Guenoche and Manson. According to the Chapman-Jouguet theory, the velocity is expected to decrease at lower initial pressure because of increased dissociation of the products. Mooradian and Gordon observed that the difference between experimental and theoretical velocities at any initial pressure, expressed as a fraction of the theoretical velocity, was inversely proportional to the initial pressure. If it is assumed that the effect of the tube wall increases as the thickness of the detonation wave (reaction zone) increases and that the latter increases as the pressure decreases, then Mooradian and Gordon's experimental results are indirect indications of diameter effects. It has been firmly established by recent investigators (48, 119, 120, 182) that the wave thickness varies inversely with the square of the initial pressure. Thus, it would appear that Mooradian and Gordon's results also add support to Zeldovich's (320, 321, 322) analysis.

Fay and co-workers (118, 120, 122) and also Kantrowitz argue

that although the Zeldovich theory ( 320, 321, 322) explains in a qualitative way the effects of tube diameter and initial pressure on the detonation velocity, i. e., "velocity deficit," the physical picture of the flow proposed by Zeldovich was incorrect. Fay recently advanced a quantitative explanation of the velocity deficit, considering the growth of the viscous boundary layer on the tube walls and its effect upon the flow in the reaction zone. Fay contends that the boundary layer displacement effect within the reaction zone produces a uniform flow divergence throughout the detonation front. Based on his analysis, Fay proposes a two-dimensional model of gaseous detonation in finite diameter tubes where the wave is stabilized by boundary layer effects. Fay ( 118) finds relatively good agreement between measured "velocity deficits" and those predicted on the basis of his two-dimensional model. Fay and co-workers ( 118, 120) also used their two-dimensional model in an attempt to explain the detonation wave densities measured by Duff, Knight and Rink ( 95 ), as well as the double waves in hydrocarbon-oxygen mixtures discovered by Cher and Kistiakowsky ( 47 ), and the short-time constancy of the pressure behind a detonation as determined by Edwards, Williams and Breeze ( 103 ). Fay based his arguments on the fact that the flow is slightly supersonic behind the detonation wave due to the growth of the boundary layer. Recent tests by Jaarsma and Fuhs ( 163 ) adds support to the existence of a two-dimensional flow region behind the Chapman-Jouguet plane,

as postulated by Fay. This investigator believes that the two-dimensional model postulated by Fay has considerable merit and deserves serious consideration.

## F. Stability of the Detonation Wave

### 1. Detonation Wave Structural Instability

The question has arisen recently as to whether there really is a steady (in the usual aerodynamics sense) detonation wave. The existing theories, either one- or two-dimensional all refer to steady flow. Their success in predicting velocities, pressures and densities stem from the fact that, on the basis of a space or time average, they do not violate the conservation laws. Thus, the Chapman-Jouguet theory holds quite well for the macroscopic description of the steady detonation wave where the reaction zone can be considered as a true plane discontinuity and the flow steady. These are perfectly valid assumptions for many real detonation conditions; i. e., atmospheric pressure and above, large diameter tubes, near stoichiometric mixtures. However, if one is interested in processes whose extent in space is on the order of a millimeter and in time is on the order of a microsecond, recent experimental evidence has indicated that the detonation wave, from a microscopic viewpoint, can no longer be regarded as a one-dimensional steady wave.

Recent schlieren pictures by Opel (120, 122, 234) and inter-

ferograms by Martin and White ( 218, 219) of detonation waves in stoichiometric hydrogen-oxygen mixtures have indicated that at low subatmosphere initial pressures, detonation waves proceeding at their characteristic Chapman-Jouguet velocities are apparently not steady, and have a non-uniform random structure on a scale comparable with the wave thickness. This is true even for waves of several millimeters in thickness ( 14, 119, 120, 234 ). Under these low pressure conditions, the combustion zone is easily discernible. The front is definitely wrinkled so that the collision centers and reaction fronts are intermingled, apparently in a random fashion over the cross-section of the wave. Since the photographs were taken at a fraction of a microsecond exposure, they represent essentially instantaneous conditions of phenomena. They show the "turbulent" or non-steady nature of the reaction zone under these conditions. This indicates an extremely intimate coupling between the reaction zone and the shock wave which appears to result in this characteristic instability of the detonation front ( 218, 219 ). The schlieren photographs ( 120, 122, 234 ) show that the density fluctuations persist down to the discrimination distance of the schlieren system ( about 1 mm. ) when the reaction zone is shortened by increasing the initial pressure. The density fluctuations within the reaction zone are completely absent in the wake, except for regular large scale variations in the transverse direction, reminiscent of spinning detonations.

Opel (120, 122, 234) notes that when the reaction zone thickness is small compared to the tube diameter, the detonation wave is plane. However, on a scale comparable to the wave thickness, the flow appears to be far from one-dimensional and steady. At sufficiently low pressures, the wave thickness becomes comparable with the tube diameter, and the detonation front is no longer plane. Opel (120, 122, 234) indicates that sometimes regularities in the structure appear clearly associated with the lateral dimension of the tube and perhaps with spinning detonation. Martin and White (218, 219) found that a low-pressure hydrogen-air or hydrogen-oxygen detonation has an irregular front, plane only on the average. They found that the period of unstable oscillation, and therefore the magnitude of departures of the wave front from planarity, increase with the reaction zone thickness. Hence, they became greater at the lower pressures. Martin and White also observed that when the transverse scale of the disturbance approaches the tube dimension, reaction cannot be maintained, and the wave will not propagate as a detonation. Hornig and Levett (159) showed that the detonation shock front in a lean hydrogen-oxygen ( $H_2 + 3 O_2$ ) mixture at initial pressures of 100 to 200 cm. is flat to  $3^\circ$ . Denisov and Troskin (79) showed that at initial pressures up to 90 cm. in stoichiometric hydrogen-oxygen mixtures, interactions between shock wave and reaction zone distorted the wave front. Duff (91) inferred from these observations of Hornig (159) and Denisov (79) and found from his investigations

( stoichiometric hydrogen-oxygen mixtures at initial pressures up to 160 cm. ) that the interactions in the wave front, although still present, become so weak at higher pressures that they produce only small changes in the inclination of the primary shock wave. Chesick and Kistiakowsky ( 48 ), working with pure shocks in mixtures of xenon and polyatomic gases and with detonations in hydrogen-oxygen-xenon (  $2\text{H}_2 + \text{O}_2 + 1/2 \text{Xe}$  ) mixtures at initial pressures from 20 to 70 mm. , found that pure shock wave fronts have almost negligible distortion as compared to detonation wave fronts at these low pressures. They further conclude that the longer the reaction zone is, either because of lowering of the initial pressure or of a change in gas composition, the more curved is the wave front. At very low pressures the wave front was exceedingly distorted, indicating the occurrence of spinning detonation. Duff ( 91 ) and Roshko ( 124 ) observed that at very low initial pressures the wave is definitely non-planar. Duff and Knight ( 93 , 120 ) showed that gross distortions of the shock front occurred in a spinning detonation.

## 2. Detonation Limits

The subject of detonation limits is outside the scope of this investigation. However, because of its close relationship with some of the phenomena already discussed, some general comments will be made in this review. The classical theory of Chapman and Jouguet and the extended theories of von Neumann, Döring and Zeldovich and

others, since they are based primarily on thermodynamic relationships, do not predict whether a mixture will or will not detonate. In fact, it would appear that any gas which can react exothermically could detonate if the conditions explicit in the theory were fulfilled.

The limits of detonability, i. e. , composition, pressure, tube diameters, etc. , where no steady detonation can be supported, has been looked into by a number of investigators. Wendlant ( 308 ) attempted to establish a criteria for a stable detonation wave, using the constancy of the detonation velocity in the first and last portions of a long detonation tube. Recently, a number of investigators have attempted to rationalize detonation limits on the basis of kinetic and relaxation phenomena occurring in the steady wave process. Gordon, Mooradian and Harper ( 135 ) attempted to predict detonation limits on the assumption that detonation occurs when a specified temperature is reached downstream of the shock wave which precedes the combustion wave. Belles ( 14, 15 ) based his predictions of the detonation limits on the application of explosion criteria to establish the conditions which would result in detonation. Patch ( 243 ) compared the constant temperature criteria of Gordon, et. al. ( 135 ) with the explosion criteria of Belles ( 14, 15 ). In addition, he included the effects of various degrees of rotational and vibrational relaxation on both criteria.

Lewis and von Elbe (201) indicate that the combustion limits are normally wider than the detonation limits. Belles (14, 15) indicates that the limits of detonability will widen at reduced pressures. Belles also states that inert gases affect the predicted limits because of variation in specific heat ratio and in chain-breaking efficiency. Carbon dioxide, he says, should contribute to narrowing the limits. Argon-containing mixtures should lower the lean detonability limit. He notes that inert gas effects show up chiefly in the predicted lean limits, and that the rich limit is mainly governed by the amount of oxidizer available to burn fuel and produce energy for driving the shock wave. In spite of the significant progress made, no completely satisfactory quantitative theoretical treatment of the limits of detonability is available yet.

### 3. Development of Plane Detonation Waves

An understanding of the transition from deflagration to detonation in plane detonation waves is an important part in understanding the overall picture of detonation phenomena. However, since it is outside the scope of this investigation, only general comments will be made here. Oppenheim and Stern (239) have recently presented a comprehensive review of the literature pertaining to both theoretical and experimental investigations on the predetonation region and transition region. Most of the experimental information concerning the develop-



ment of detonation has been provided by photographic observation of the phenomena, although other techniques have been used with good success. Among the most recent contributions to the phenomenological description of the development of detonation are those due to Schmidt, Steinicke and Neubert ( 279 ), Turin and Huebler ( 300 ), Evans, et. al. ( 112 ), Bollinger, Edse, et. al. ( 21, 22, 23, 25 ), Brinkley and Lewis ( 37 ), Cook, et. al. ( 65 ), Martin and White ( 218, 219 ), Kistiakowsky, et. al. ( 176, 185 ), Zeldovich ( 319, 320, 321, 322 ), Shchelkin ( 284, 285 ), Sokolik ( 290 ) and Oppenheim and co-workers ( 142, 189, 190, 191, 192, 235, 237, 238, 239, 240 ).

Most of the older analytical studies of processes leading to the establishment of a detonation wave have been based on a simplified one-dimensional gas-dynamic model. The propagating waves have been considered as finite discontinuities with transport effects and induction or relaxation phenomena neglected. However, some advanced analytical treatments have been attempted such as those of Oppenheim and co-workers ( 142, 189, 190, 191, 192, 235, 237, 238, 239, 240 ), Adams and Pack ( 1 ), Popov ( 257 ), Jones ( 166 ), and Tayler and Tonkin ( 293 ). These studies deal primarily with wave interaction phenomena, one of the most important features of unsteady flow processes.

In some of these analysis the model of the combustion system

developing into a detonation is considered to be an unsteady double discontinuity, with the two discontinuities corresponding to the leading shock and the following combustion fronts. This is different from stable detonation which can be represented by a steady-state single discontinuity system. A quantitative basis for the calculation of the characteristic detonation formation properties is not available yet.

#### G. Review of Analytical Work

Both manual and digital computer methods for theoretically calculating detonation parameters have been reported in the literature by a number of investigators including Lewis and von Elbe (199), Jost (169), Manson (216), Tits (294), Bollinger (24), Edse (101), Wolfson and Dunn (99, 100, 316, 317), Eisen, Gross and Rivlin (105), Zeldovich and Ratner (323), and Cook, et. al. (59, 63). In the majority of cases, the calculation methods are concerned with the idealized steady plane Chapman-Jouguet detonation, assuming chemical and thermodynamic equilibrium in the detonation products, ideal gas behavior, infinite reaction rates, and no transport effects. Eisen's, et. al. (105) method is concerned with the calculation of strong and weak as well as Chapman-Jouguet detonation properties. The calculation of the Chapman-Jouguet detonation parameters, being a thermohydrodynamic problem only, is straight forward. The idealized detonation velocity and other parameters

can be derived from the thermodynamic functions of the initial and final states of the detonable mixture without knowledge of the mechanism by which the initial products are transformed into the final detonation products. All the computational methods are basically quite similar, although the numerical methods of solution have varied. These methods are concerned primarily with the solution of the Chapman-Jouguet relationships; i. e., equations of conservation of mass, momentum and energy across the shock discontinuity, chemical equilibrium of the product flow, an equation of state (usually the ideal gas law), and the fact that the product flow Mach number is exactly equal to one (the Chapman-Jouguet postulate). The equations to be solved consist of a large set of nonlinear algebraic equations which necessitate the utilization of iterative procedures to obtain the equilibrium product gas composition, temperature and other parameters at the Chapman-Jouguet condition. Thus it can be seen that although the calculations are straight forward, they are rather laborious.

Most of the calculation procedures use dimensional nomenclature, though a few use non-dimensional nomenclature. In some methods (169, 199, 216, 294, 323) use was made of an approximation involving mean specific heats in the conservation of energy equation. Edse (101) and Wolfson and Dunn (99, 100, 316, 317) eliminated this approximation by using exact thermodynamic functions of the

gaseous mixtures at the initial and final states. Condensed phases in the reaction products; e. g. , solid carbon, solid oxides, etc. , are neglected in the majority of the calculation procedures. Cook ( 59, 63 ) however, takes into consideration the influence of solid carbon and other condensed phases on the detonation parameters. Some of the calculation procedures are based on the use of the "frozen" speed of sound while others utilize the "equilibrium" speed of sound ( 24, 105 ). Edse ( 101 ) eliminated the conflict between the choice of the proper specific heat ratio,  $\gamma$  , to use in the expression for the sound speed. He based one of his methods of calculation on the Chapman-Jouguet hypothesis that the tangent to the equilibrium Hugoniot curve ( see Figure 1 ) drawn from the initial condition point yields the pressure and specific volume of the product gas for the stable detonation wave. The Chapman-Jouguet hypothesis defined in this manner is utilized in this dissertation to calculate the Chapman-Jouguet detonation parameters ( See Appendix III ).

Edse ( 101 ) and others point out that the calculated values of the detonation parameters obtained by using the procedures based on the simplified Chapman-Jouguet theory represent ideal solutions. In actual gaseous detonations, these values usually will not be fully attained because of unavoidable thermal losses, incomplete reactions, and friction between the gas and the wall. Therefore, the calculated values will normally be somewhat higher than the experimental values.

The difference between these values will vary between cases. It is pointed out, however, that it is possible for the experimental values to exceed the theoretical values in certain conditions due to frozen degrees of freedom in the molecules or due to deviation from chemical equilibrium. The influence of these effects has already been discussed in Part IID-3 of this section.

Several graphical procedures for presenting and computing detonation parameters have been published including those of Manson (216), Markstein (217), Evans (107) and Wolfson and Dunn (99, 316).

#### H. Experimental Techniques for Determination of Detonation Parameters

##### 1. Detonation Wave Velocity

Several methods have been employed for determining detonation velocities, and most of these methods are capable of yielding quite accurate data. Berthelot and Vieille (19) in 1882 were the first to obtain fairly good values of the wave velocities by means of a chronoelectric method. This same principle is still used today with refinements afforded by the application of modern electronic techniques to enable wave velocities to be measured to a high degree of precision; e. g., the pin-chronograph and the pin-oscillograph methods (21, 28, 42, 46, 175, 186, 187, 224, 225, 262). This technique

involves the use of ionization probes mounted in the detonation tube at a measured distance apart. The probes either make or break an electric circuit on arrival of the detonation wave, thereby actuating a timing mechanism. Wave detection by the ionization probes is made possible by the conductivity of the flame gas due to its ion content, thus each probe is made conductive when the detonation wave passes it. Instead of ionization probes to detect the detonation wave, Wendlandt (308) used a wire or metal-foil type probe which ruptured upon passage of the detonation wave, thereby interrupting a current for timing purposes. In this system it is necessary that the probes be identical so that the rupture process occurs in equal time intervals at both stations. Pressure gages, such as piezoelectric crystal or condenser-type probes capable of responding to high frequencies, have also been used by Kistiakowsky and co-workers (17, 18, 178, 179, 180), Gordon (132, 133, 223), and others to detect the passage of the detonation wave. In each of these methods, the velocity is determined by accurate measurement of time intervals and distance between probes. One unfortunate feature in the use of any type probe is that it normally will be in direct contact with the detonation wave as it passes the probe station. Thus, it is exposed to the highly destructive effects of the explosive process. The design of an ionization probe or pressure transducer capable of withstanding the pressures and temperatures accompanying the detonation phenomena poses quite

a problem, especially for high initial pressure conditions and for oxidizing mixtures. Boyd and Fagan (33), Cook and co-workers (62), and others utilized a microwave technique to measure the detonation velocity. This method is based on the reflection of microwaves from the ionized detonation front. It was found to be particularly useful in studies where the detonation velocity varies with time (33). Mallard and LeChatelier in 1900 (214) determined the detonation velocity by recording the burning process on moving photographic plates. Since that time considerable advancements have been made in high-speed photography. These include the development of high-speed rotating drum and rotating mirror streak framing cameras capable of obtaining direct and schlieren photographs of high-speed detonation waves with microsecond time resolution (60). One of the difficulties with the photographic process is that the detonation tube must have a window mounted in it throughout the desired observation length. At atmospheric or moderate pressures, observation windows are not too much of a problem. However, above 10-atmospheres initial pressure, the requirements for tube and observation window strength become severe. The main disadvantage of photographic determination of detonation velocities is that the instantaneous velocity has to be determined from the tangent to the luminous trace. This limits the accuracy obtainable.

## 2. Detonation Wave Pressure

In contrast to detonation wave velocity measurements, the measurement of detonation pressures is much more difficult. This is due to its very transient nature, i. e., pressure rise to peak value in less than  $10^{-7}$  sec. ( 163 ), and also to its high magnitudes. Also the sensor used to measure the pressure has finite dimensions of much greater magnitude than the shock front preceding the detonation wave or the detonation wave itself under normal conditions; i. e., wave thickness less than 1 mm. at atmospheric pressure. This permits at best the measurement of average pressure, except possibly at the Chapman-Jouguet plane where the time available for measurement is greater. Techniques for the direct measurements of peak pressure in the wave front as predicted by the NDZ "spike" theory, the detonation wave front impact pressure, and even the Chapman-Jouguet pressure, are still far from satisfactory. Early work on detonation pressure measurement produced only a crude and uncertain measure of the peak pressures generated in detonation waves. Thus, in 1894 Dixon and Cain ( 84) attempted to estimate the pressures generated from known static pressure strengths of glass tubes which were just fractured by the impact of the wave. Cambell, Littler and Whitworth ( 44) measured the detonation pressure by determining the thickness of a statically calibrated metal foil placed across the end of the detonation tube which was just capable of being



broken by the wave. The results of both investigations were very approximate since the dynamic conditions in the pressure effect of the wave front are not comparable with those at static pressure ( 134, 170, 223 ). Similarly, the results of the crusher gage experiments of Rimarski and Konschak ( 266 ) and Henderson ( 149 ) must be regarded as unreliable. Among the best of the detonation pressure measurements to date are those of Gordon and co-workers ( 132, 134 ), Davies, Edwards and Thomas ( 75, 76 ), and Edwards, Williams and Breeze ( 103 ). Gordon, et. al. employed a small tourmaline piezoelectric crystal in conjunction with a cathode ray oscilloscope display. The crystal was mounted in an oil-filled tube-mounted at right angles to the detonation tube in such a way that the oil surface was flush with the inside of the detonation tube. The purpose of the oil column was to dampen out high-frequency crystal vibrations ( "ringing" ) in order to permit measurement of the "static" detonation pressure rather than the "dynamic" pressure. Results from preliminary work done at Syracuse University using similar equipment seem to indicate that Gordon's method is not very satisfactory and that an average pressure is recorded by this means rather than the true peak pressure ( 211, 212 ). Also, the method used by Gordon, et. al. to calibrate their pressure transducer is not considered to be very reliable by this investigator. Surprisingly enough, however, Gordon obtained good agreement between measured and theoretical values of side-wall

and reflected pressures for a few compositions. Gordon makes no claim for great accuracy of his data. It is possible that the close agreement obtained between experiment and theory was due partially to a fortuitous cancelling of errors inherent in this method. Davies, et. al., (75, 76) used both crystal quartz gages and the Hopkinson pressure bar method in the electrical form devised by Davies (75). Preliminary results obtained appeared promising. However, it was determined that a more satisfactory gage design was required before completely reliable pressure measurements could be achieved. Edwards, et. al., (103) used an improved version of the Hopkinson pressure bar method, employing an X-cut quartz disk to measure the average stress over a 1/4- and 1/2-inch diameter duralumin rod. Good agreement was obtained between experimental and theoretical values of Chapman-Jouguet pressure in a number of cases. Macafee (212) used a flush-mounted strain gage pressure transducer in conjunction with a cathode ray oscilloscope to measure static and reflected detonation pressures. McGill and Luker (211, 212) used both quartz piezoelectric and strain-gage transducers together with a cathode ray oscilloscope display to measure reflected detonation wave pressures. In the piezoelectric sensing device the reflected pressure was transmitted by a piston to the crystal. No claim for accuracy is made by McGill and Luker. In fact they indicated that the experimental instrumentation used was not satisfactory for the accurate measurement of the detonation wave pressure.

The Chapman-Jouguet detonation pressure is accurately defined by the thermohydrodynamic equations:

$$p'' = \rho' D u'' + p' \quad (12)$$

$$u'' = (1 - \rho'/\rho'') D \quad (13)$$

Hence, a measurement of detonation velocity and density is adequate to determine the particle velocity,  $u''$ , as well as the Chapman-Jouguet pressure,  $p''$ . A measure of the particle velocity together with the detonation velocity is sufficient to determine the Chapman-Jouguet pressure.

### 3. Detonation Wave Density

Measurement of detonation wave density has been attempted by a number of investigators. Schell (278) determined the density behind the detonation wave front from densitometric traces of flash radiographs. Kistiakowsky and co-workers (47, 48, 177, 182, 184), Duff and Knight (187), Knight and Venable (188), and others utilized the absorption of soft X-rays to measure densities behind gaseous shock and detonation waves; i. e., time-resolved continuous (or streak) radiography. Kistiakowsky, et. al., used the time-resolved density measurements to deduce pressure characteristics through the reaction zone to the Chapman-Jouguet plane and back into the products of detonation in gaseous explosives.

### 4. Detonation Wave Particle Velocity

Various methods of direct measurement of the mass flow velocity

(particle velocity) of the products behind pure shock fronts and detonation wave fronts have been studied, primarily to enable calculation of the detonation pressure. Payman, Woodhead, and Shepherd (245, 246) used schlieren photography with a wave speed camera. Clark and Seely (53) obtained estimates of particle velocity in the detonation of solids by X-ray photography of special so-called "zebra" charges containing alternating layers of explosives with and without incorporated lead nitrate. Mallory and Jacobs (215), Duff and Houston (92), Deal (77), and others determined the initial free surface velocity imparted to thin metal plates in shock-loading of the plate by the detonation wave. This permitted estimation of the reaction zone length and the Chapman-Jouguet pressure.

#### 5. Detonation Wave Product Gas Composition

Attempts have been made to measure detonation product gas composition without much success to date (197). Robertson and Garner (267) tried to analyze the gases formed when detonation occurred in a lead block enclosed in a sealed bomb. However, the results obtained cannot be referred (145) to the zone immediately behind the detonation wave since the various equilibria involving  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$  etc., are only frozen after extensive expansion has occurred (167).

#### 6. Detonation Wave Temperature

A number of attempts have been made to measure detonation

temperature. However, to date none has been successful (41, 147, 151, 197, 198). Cook (61) summarizes the difficulties in measuring detonation temperature as follows: (1) The temperature designated as detonation temperature is a very transient one, similar to the detonation peak pressure, its duration being of the order of microseconds or less. (2) At the high pressures existing at the Chapman-Jouguet plane, the products of detonation are not transparent so that one has difficulty viewing the region of interest. (3) Temperatures are in the range of  $2000^{\circ}$  to  $6000^{\circ}$  K. which are not easily measured even were it possible to observe the region of interest directly. (4) The reaction zone is a highly conducting region and is in general accompanied by strong chemiluminescence. Hence there is a question even regarding the meaning of "temperature" in the reaction zone at least. (5) Means for obtaining information from the region of interest without interference from other regions, and from the interfaces between these regions and the measuring device poses a serious problem. Harris (147) discusses these various problems and mentions various methods which look the most promising for temperature measurement including: photo-multiplier color pyrometer, image-orthicon spectrograph, and image-converter spectrograph. Recently Warner and Swasey (297, 298, 299) investigated the use of a unique optical technique with microsecond response characteristics to measure the Chapman-Jouguet temperature in gaseous detonations. The technique involves the measurement of infrared monochromatic emission and absorption

radiation. This method appears to offer some interesting possibilities.

It would appear, then, that accurate time-resolved measurement of temperature can be achieved. The main problem, however, is not concerned with the instrumentation techniques, time resolution and accuracy of temperature measurements, but with the interpretation of the actual temperatures measured. Ubbelohde (198) indicates that it may not be possible to define a detonation "temperature" as a unique parameter defining the statistical distribution of energy among the various degrees of freedom in the system, since these distributions may show relaxation times comparable with the reaction time.

#### I. Theoretical Calculations and Experimental Measurements of Detonation Parameters

A great number of experimental measurements of detonation wave properties, utilizing shock and detonation tubes, and many theoretical calculations of detonation wave parameters have been made for various gas mixtures since the discovery of detonation phenomena. As was indicated previously, in many cases quite satisfactory agreement was obtained between experimental and theoretical velocities calculated by means of the Chapman-Jouguet equations. No attempt will be made in the review to cover all the gaseous mixtures and conditions for which detonation results have been reported. Instead, coverage will

be made of calculations and data reported on gas systems pertinent to the present investigation. (An excellent review of the experimental and theoretical work on detonation up to 1961 is presented by Lewis and Von Elbe (199)).

As inferred previously, a considerable amount of labor is involved in the theoretical calculation of detonation parameters. Because of this, until recently, most of the published reports covered relatively simple two element reacting chemical systems; e. g., hydrogen and oxygen. All but the most important reaction products were neglected (24, 47, 48, 100, 101, 126, 127, 134, 177, 182, 184, 317). Unfortunately, most of the authors presented only calculated values of detonation velocity, temperature and pressure. In many reports there is inadequate description of the sources of thermodynamic data. In most cases the chemical composition of the product gases is not given. This makes comparison of data from various sources difficult. A few reports containing complete detonation calculations have been published, however, of a two or more element system (105, 171, 186, 195, 216). Recently electronic digital computers have been utilized to solve the more complex systems with high accuracy (105, 178, 180, 186).

Ideally, a thorough study of detonation phenomena would include direct measurement of detonation velocity; pressure, density and

temperature distribution in the region immediately behind the shock front; product gas composition, and mass flow velocity of the reaction products behind the shock front, over a wide range of initial conditions for many different gaseous mixtures. Only the first three of these quantities have been measured with any degree of success for a limited number of mixtures, mostly at or near ambient initial temperature and pressure. Discussion in this review will be concentrated primarily on reported measurements of these three quantities in mixtures pertinent to this investigation.

#### 1. Detonation Velocity Measurements and Detonation Calculations

Dixon ( 82, 83 , 85 ) measured detonation velocities in mixtures of hydrogen-oxygen at 10°C and 100°C. over a pressure range from 200 to 15 00 mm. mercury. Lewis and Friauf ( 195 ) reported calculated and experimental detonation velocities in pure hydrogen-oxygen and hydrogen-oxygen mixtures with additives of nitrogen, helium and argon at 1 atmosphere initial pressure and ambient temperature. Kistiakowsky and co-workers ( 17, 18, 47, 48, 178, 180, 181, 182, 183, 184, 186 ) measured and calculated detonation velocities in similar mixtures as well as in mixtures of cyanogen-oxygen, acetylene-oxygen, and carbon monoxide-oxygen at ambient and subatmospheric initial pressures and initial temperature of 25 °C. in various tube diameters.( The data of Kistiakowsky, Berets and Green ( 17 ) are considered to be the best available for detonation waves in hydrogen-oxygen-diluent systems at these initial conditions ).



Hoelzer and Stobaugh (157) measured detonation velocities in hydrogen-oxygen mixtures and ethane-oxygen mixtures over a pressure range of 1 to 10 atmospheres for several compositions. Cannon and Jewell (45) measured detonation velocities in hydrogen-oxygen and ethane-oxygen at initial pressure of 1 atmosphere over an initial temperature range of 30°C to 180°C. Bennett and Wedaa (16) reported detonation velocities in stoichiometric hydrogen-oxygen and acetylene-oxygen mixtures at initial pressures from 10 mm to 400 mm. mercury. Moyle, Morrison and Churchill (225) measured and calculated detonation velocities over an initial temperature range of 160°K to 480°K, a pressure range from 0.5 to 2 atmospheres, and a composition range from 0.25 to 0.78 mole fraction hydrogen in hydrogen-oxygen mixtures, for various tube diameters. Gealer and Churchill (126, 127) calculated and measured detonation velocities in hydrogen-oxygen mixtures and calculated detonation and impact characteristics for these mixtures over an initial pressure range of 14.4 to 1000 psia and compositions from 0.40 to 0.80 mole fraction molecular hydrogen. Eisen, Gross and Rivlin (105) calculated detonation parameters for twelve hydrocarbon-air mixtures as well as hydrogen-oxygen and hydrogen-air mixtures at an initial temperature of 537°R. and initial pressure of 1 atmosphere, assuming both "frozen" and "equilibrium" sound speeds. Bollinger, Edse and co-workers (24, 26) calculated detonation wave parameters for hydrogen-oxygen mixtures at initial temperatures of 40°C and

initial pressures of 1 and 25 atmospheres. They assumed no chemical reaction in the shock front and considered both frozen and varying specific heats. Manson (216), Tits (294), Breton (35), Jouguet (171, 172, 173), Bone, Fraser and Wheeler (29, 30, 31, 32), Laffitte (193), and others measured and calculated detonation velocities for hydrogen-oxygen mixtures at ambient initial temperatures and 1 atmosphere initial pressure. Belles and Ehlers (15) measured and calculated detonation velocities and Mach numbers for hydrogen-oxygen-argon, hydrogen-oxygen and hydrogen-air mixtures at initial pressures of 25 to 50 mm. mercury.

## 2. Detonation Pressure Measurements

Dixon and Cain (84) and Cambell, Littler and Whitworth (44) attempted to estimate the "static" or side-wall detonation pressure in hydrogen-oxygen mixtures at ambient initial pressure and temperature. Cambell, et. al., (44), also observed that the pressure in the transition region just preceding the formation of the stable detonation wave was about twice as high as the pressure reached after the stable detonation wave was fully developed. Rimerski and Konschak (266) and Henderson (149) measured detonation pressures in acetylene-air and methane-air mixtures respectively, at 1 atmosphere initial pressure. Gordon and Mooradian (134, 223) extended the work of Gordon (132) and measured and calculated detonation velocities for the same gaseous mixtures over an initial pressure range of  $1/4$  to 3 atmospheres. They

also measured and calculated detonation pressures as well as velocities for stoichiometric hydrogen-oxygen and stoichiometric hydrogen-oxygen-argon ( $2\text{H}_2 + \text{O}_2 + 13\text{A}$ ) mixtures over an initial pressure range of 1/2 to 2 atmospheres. McGill and Luker (210, 211) measured and calculated detonation wave velocities and impact pressures of hydrogen-oxygen-water (saturated) mixtures over an initial temperature range of  $298^\circ$  to  $473^\circ\text{K}$ . and an initial pressure range of 1 to 60 atmospheres. Macafee (212) measured and calculated values of detonation "impact" and "static" pressures for the same mixtures at initial pressures from 1 to 3 atmospheres at an initial temperature of  $100^\circ\text{C}$ ., and from 1 to 40 atmospheres at an initial temperature of  $200^\circ\text{C}$ . Edwards, Williams and Breeze (103) measured detonation velocities and "static" and "impact" pressures and computed detonation parameters and shock wave peak pressures (von Neumann "spike") in the detonation wave front for hydrogen-oxygen mixtures at ambient initial pressure and temperature.

### 3. Detonation Density Measurements

Kistiakowsky and co-workers (47, 48, 177, 182, 184) measured the variation of density with positions in the detonation wave in various gaseous mixtures, including hydrogen-oxygen mixtures with additions of krypton or xenon over an initial pressure range of 20 mm. to 1 atmosphere. In particular Kistiakowsky and Kydd (182) reported they obtained data which supports the Chapman-Jouguet theory.

Duff and Knight (93) measured and calculated densities in acetylene-oxygen mixtures at subatmospheric initial pressures. Duff, Knight and Rink (95) calculated and measured detonation wave velocity and density in hydrogen-oxygen-krypton mixtures and other mixtures at 60 cm. initial pressure.

#### 4. Miscellaneous Pertinent Measurements and Data

Breton (35) and Jones and Kennedy (165) give inflammability and detonation limits for hydrogen-oxygen mixtures at atmospheric pressure; i. e., inflammability limits: 4.65% to 93.9% hydrogen; detonation limits: 15 to 90% hydrogen. It would appear reasonable that the detonation limits would widen as the initial pressure increases by analogy to the effect of initial pressure on the inflammability limits (165, 210). Laffitte (193) investigated the effect of tube diameter and the effect of initial temperature over a range of ambient to 360°C on the detonation induction distance in hydrogen-oxygen and other mixtures. Dumanois and Laffitte (97) investigated the influence of initial pressure over the range of 1 to 6.5 atmospheres on the detonation or induction distance in stoichiometric hydrogen-oxygen mixtures. Bollinger, Edse and co-workers (21, 22, 23, 25, 26) extended investigations on detonation induction distances in gaseous mixtures. They reported measured detonation induction distances in stoichiometric hydrogen-oxygen mixtures with additives of carbon dioxide, argon, helium and nitrogen at initial pressures from 1 to 5

atmospheres and initial temperature of 40°C., and in other mixtures at initial pressures from 1 to 25 atmospheres and initial temperatures of 40°C and 200°C. Also reported were limited measurements of steady-state detonation velocities for several of these mixtures. However, no claim of great accuracy is made for the reported velocity values. From Bollinger's, et. al. limited data on detonation velocities in hydrogen-oxygen-diluent mixtures, it would appear that the measured detonation velocity at the higher initial pressures ( 5 atmospheres) was lower than that at atmospheric pressures. This result is contrary to that reported by Bollinger, et. al. for hydrogen-oxygen mixtures without additives and is contrary to what might be expected by this investigator. Based on the results of the investigations on detonation induction distances ( 26 ), it would appear that the induction distance: ( 1 ) increases with increased diluent composition, and is affected the most by carbon dioxide and the least by argon; ( 2 ) decreases with increase in molecular weight of the unburned gas; ( 3 ) decreases with increase in initial pressure; ( 4 ) increases with increase in initial temperature; ( 5 ) increases with increase in tube diameter; ( 6 ) increases with increase in mixture fuel percentage.

#### J. Evaluation of Previous Research on Detonation Phenomena

As a consequence of the literature review, it is apparent that much work, both theoretical and experimental, remains to be done before we

can claim to have a completely satisfactory understanding of detonation in gaseous mixtures. Far from complete is the thorough understanding of the detonation wave structure; e. g., wave thickness, shape, stability. Additional experimental and theoretical study on the interconnection of the combustion kinetics and transport and viscous boundary layer effects on the detonation wave properties is necessary to achieve this understanding. A number of theories and models of the detonation wave structure have been postulated. Each stipulates that the Chapman-Jouguet plane is located at the completion of the reaction zone (See Section II-E). However, to date there has been no unambiguous evidence which has conclusively proven the validity of any one theory or model. Although evidence points towards the model of detonation postulated by von Neumann, Düring and Zeldovich (88, 304, 320, 322) for ideal steady plane detonation waves, the sharp "spike" of the magnitude predicted by the NDZ theory has never been observed. Additional research in this area appears warranted, with special consideration being given to the role of transport effects as well as to viscous boundary layer effects, i. e., two-dimensional detonations.

Considerable additional theoretical and experimental work appears to be required also in order to explain quantitatively the process which occurs during detonation build-up; i. e., predetonation and transition regions.

Investigations pertaining to detonation wave structure can best be accomplished at low sub-atmospheric initial pressure conditions. These are optimum conditions for observing the wave structure. However, even under these favorable conditions, quantitative determinations of pressure, density, etc., are severely limited because the time and space resolution of present-day instrumentation is apparently not adequate to permit measurements of the wave front (von Neumann "spike") and in the reaction zone, even at very low initial pressures. Also the influence of viscous boundary layer (two-dimensional) effects, heat loss and other transport effects, effects due to non-attainment of chemical and/or thermal equilibrium at the Chapman-Jouguet plane, and wave instability and non-uniformity, become more prominent as the thickness of the wave increases (initial pressure decreases). These effects, either individually or combined, would make it very difficult, if not impossible, to evaluate quantitatively the validity of the Chapman-Jouguet theory under these conditions.

Some work has been done on determination of the proper velocity of sound; i. e., "frozen" or "equilibrium," which should be used in the theoretical calculations of detonation wave properties (See Section II D-4). However, to date this question has not been satisfactorily resolved. Therefore, the uniqueness of the definition of the Chapman-Jouguet point is still undetermined. Additional investigation appears

warranted to clarify this situation. The majority of work pertaining to steady detonation waves has involved the study of the influence of initial gas composition on the detonation velocity at or near ambient initial temperature and pressure. Very little experimental or theoretical research has been carried out on the influence of additives, either inert or chemically reactive, on the values of the detonation parameters or on the mechanism of detonation. The studies made were confined to ambient initial temperature and low initial pressures. A small number of detonation wave pressure and density measurement have been made at ambient initial temperature and ambient or low initial pressure. The pressure measurements, for the most part, are of doubtful accuracy. Very little theoretical or experimental work has been accomplished on the influence of initial pressure and initial temperature on the values of the detonation parameters and on the mechanism of detonation. Close agreement has been found between experimental values and calculated values based on the classical Chapman-Jouguet theory for many low pressure gaseous detonations. However, none of the various postulated models of detonation or the Chapman-Jouguet thermohydrodynamic theory has been thoroughly tested, and the detonation properties and mechanical shock wave parameters preceding the detonation wave front have not been determined, over wide ranges of initial pressure and temperature in gaseous detonable mixtures, with or without additives. In particular, the high pressure region is virtually unexplored; i. e. ,



above approximately 2 atmospheres to 1000 atmospheres. Additional investigation in this area is certainly warranted.

Investigations of detonation phenomena at elevated initial pressures offers some unique advantages, but also has certain limitations. The reaction zone width, being inversely proportional to the square of the initial pressure, becomes smaller with increase in pressure. The time available to observe internal wave structure decreases in a like manner. Thus observation of wave structure, e. g., quantitative measurements of density and pressure in the reaction zone, becomes virtually impossible with present-day instrumentation. Also, measurement of the peak pressure in the mechanical shock wave preceding the detonation reaction zone ( according to the NDZ model of detonation) is highly improbable. Also, real gas effects may become significant at the higher initial and final gas pressures. This necessitates the inclusion of real gas thermodynamic properties in the computation of detonation parameters before quantitative comparison of theoretical and experimental values can be made.

Measurements of pressure and velocity in the Chapman-Jouguet region immediately following the reaction zone at elevated pressures offer distinct advantages over such measurements at low pressures insofar as their utilization in determining the validity of the Chapman-Jouguet theory. At elevated pressures small microscopic instability

and random structural effects become insignificant due to the very small overall detonation wave width. Also energy losses due to incomplete reaction and non-attainment of thermal equilibrium should diminish at higher pressures. Heat losses to the walls and other transport property effects will diminish as the initial pressure increases. Also two-dimensional (viscous) effects should decrease as initial pressure increases, since the boundary layer thickness is inversely proportioned to the initial pressure. Thus it appears that with increase in initial pressure, the model of detonation should approach the idealized one-dimensional steady-state model postulated by von Neumann, Döring and Zeldovich. It also appears that calculated Chapman-Jouguet values should agree quite well with experimental values, provided influences due to non-ideality of the initial and product gases are considered, except under conditions where sufficient time is not available for chemical and/or thermal equilibrium to take place. This latter condition could very well occur in gaseous mixtures diluted with additives such as helium, argon, or carbon dioxide. Thus at elevated initial pressures, the Chapman-Jouguet region appears to be most prominent and most desirous to investigate. From a macroscopic viewpoint, an increase in initial pressure should increase the temperature and thereby the reaction rate. This should increase the amount of energy available for wave propagation for a given mixture by decreasing the amount of dissociation in the detonation products. This should increase the detona-

tion pressure ratio as well as the detonation velocity and temperature. The addition of inerts, such as helium and argon which are chemically identical but differ in atomic weight, to a detonable mixture should furnish an additional means for checking the validity of the Chapman-Jouguet theory since the classical theory indicates that the detonation velocity is proportional to the density of the gas mixture after combustion and to the absolute temperature reached in the wave front. Thus the velocities for mixtures with an equal number of moles of helium and argon ideally should be inversely proportional to the square root of the density of the burned gases. (This assumes, of course, that thermal and chemical equilibrium are achieved in the reaction zone). Addition of constituents, such as carbon dioxide, which can act both as a pure diluent or as a chemical reactant under certain conditions, should provide an interesting test on the validity of the Chapman-Jouguet theory, especially in cases where the carbon dioxide enters actively into the chemical reaction process. Theoretical calculations of Chapman-Jouguet detonation parameters for these cases should include solid carbon as one of the detonation products.

### III. THEORETICAL AND EXPERIMENTAL PROGRAM

#### A. Proposed Investigation and Method of Attack

On the basis of the review and evaluation of previous research on detonation presented in Section II-J, it was concluded that a study of detonation phenomena in detonable mixtures with and without additives over a much wider range of initial pressures than has been reported in the literature would be most fruitful from both an academic and a practical viewpoint. Especially, it was considered that the studies should encompass the higher initial pressure conditions for the reasons enumerated in the previous section. It was decided to measure detonation pressure in the Chapman-Jouguet plane as well as detonation velocity. This was because in many instances the velocity, or any other parameter such as pressure, density or temperature alone may not provide a sufficiently strong criterion to establish whether thermal and chemical equilibrium has been achieved in the Chapman-Jouguet plane. Further, a comparison of the detonation pressure as well as the detonation velocity with the theoretical values should provide far more sensitive criteria of the validity of the Chapman-Jouguet hypothesis itself than a measure of the velocity alone. This is because the pressure possibly is more sensitive than the velocity to initial pressure, temperature, final product composition and other variables. It was decided not to attempt to resolve the reaction zone structure in this investigation. It was felt that no instrumentation presently available had sufficiently fast enough time and space resolution for this purpose. No such

problem was expected in the measurement of pressure in the Chapman-Jouguet plane under any initial conditions planned for this investigation. This is because sufficient time (20-50  $\mu\text{sec.}$ ) is available before the rarefaction wave spreads into the reaction zone. This permits measurements to be made with newly developed pressure measuring equipment, i. e., piezoelectric quartz crystal transducer in conjunction with electronic analog compensation to permit relatively accurate measurements of the Chapman-Jouguet pressure.

The main purpose of the present investigation, therefore, is to obtain additional fundamental understanding of the mechanism and fluid dynamics of supersonic energy release or detonative combustion in gaseous mixtures. This is to be accomplished by investigating both experimentally and theoretically the influence of additives, both chemically reactive and inert (helium, argon and carbon dioxide), on the mechanism of detonation in stoichiometric hydrogen-oxygen detonable mixtures at ambient temperature over a wide range of initial pressures, with special emphasis on high initial pressures, i. e.,  $1/2$  to 1000 atmospheres, and over a wide range of additive compositions, i. e. 0 to 50% additive. The validity of the Chapman-Jouguet thermohydrodynamic theory will be determined over this considerably more extended range of initial pressures than has been heretofore reported for these mixtures. This is to be accomplished by a critical

comparison of theoretical and experimental detonation velocity and detonation static pressure results. The experimental investigation will be limited to the use of one detonation tube with no change in geometry or internal surface and to one particular method of ignition.

#### **B. Experimental Equipment, Instrumentation and Techniques**

The high-pressure detonation test facility was designed to permit investigation of detonation wave propagation in quiescent combustible gaseous mixtures at initial pressures up to 100 atmospheres. Particular emphasis was placed on incorporating means for measuring detonation velocities and pressures under these conditions. The principal components of the installation consisted of a detonation tube, a gas handling system, an ignition system, a velocity measuring system, and a pressure measuring system. A detailed description of the experimental equipment, instrumentation and operating techniques, including photographs ( see Figs. 2 through 27) is presented in Appendix V.

#### IV. THEORETICAL AND EXPERIMENTAL RESULTS

##### A. Theoretically Calculated Detonation Parameters

Detonation characteristics of the ideal steady-state plane detonation wave at the Chapman-Jouguet condition were computed on an IBM 7090 digital computer by means of the idealized thermohydrodynamic theory of detonation ( see Appendix I through V of this dissertation for details) for the hydrogen-oxygen-additive systems being considered. The calculations covered pure stoichiometric hydrogen-oxygen mixtures admixed with helium or argon in concentrations of 10, 25, 37-1/2, and 50% by volume; and stoichiometric hydrogen-oxygen mixtures admixed with carbon dioxide in concentrations of 4, 10, and 25 % by volume. The calculations were made for each of these mixtures at an initial temperature of 300°K. and at initial pressures of 1/2, 1, 5, 10, 20, 100 and 1000 atmospheres. The detonation parameters calculated include the detonation velocity, Mach number, static and impact pressures, temperature, density and composition of the products at chemical and thermal equilibrium. Also calculated were values of the "frozen" and "equilibrium" specific heat ratios in the final mixture, the "frozen" and "equilibrium" speeds of sound, and the Mach number of the detonation wave with respect to the product gases based on the "frozen" or "equilibrium" speeds of sound. Solid carbon in the detonation products was taken into account in the calculations involving the carbon dioxide-additive mixtures.

In addition, values were calculated of the conditions existing behind a normal shock wave preceding the combustion zone and propagating into the unreacted combustible mixture at the speed of the Chapman-Jouguet detonation wave without causing any chemical reaction in the gas; i. e., the "von Neumann spike."

It would be well to point out at this time that the calculated detonation parameters are based on the idealized Chapman-Jouguet theory which neglects all losses including those due to wall effects. Thus the calculated detonation velocities and pressures obtained correspond to those which would be measured in a tube of infinite diameter. It should be pointed out also that the idealized Chapman-Jouguet theory does not predict detonation limits. Therefore, it is entirely possible that for some of the mixtures and initial conditions, the calculated data obtained may be hypothetical only since the detonation limits of composition or pressure or both may have been exceeded. More will be said about these points in Section V of this dissertation, "Discussion and Interpretation of Results."

The initial conditions and the computed values of the Chapman-Jouguet detonation and non-reactive shock parameters for each initial condition are presented in Appendix VIII, Table 1, for the pure stoichiometric hydrogen-oxygen mixtures, (hereafter normally referred to as the "basic mixture"), in Tables 2 through 5 for the basic mixture ad-



mixed with helium, in Tables 6 through 9 for the basic mixture admixed with argon, and in Tables 10 through 12 for the basic mixture admixed with carbon dioxide. The results of the theoretical calculations, as well as the experimental values of detonation velocity and detonation static pressure obtained for all mixtures and initial conditions considered in this investigation and pertinent literature values, are presented in Figs. 31 through 47; Tables 13 through 24, Appendix IX, and Table 25, Appendix X, respectively. A brief description and pertinent information pertaining to the theoretical data plotted will be given in the following paragraphs of this sub-section. Similarly, a description of the experimental plots will be given in the next portion of this section entitled "Experimental Measurements of Detonation Velocities and Pressures." The results will be analyzed and discussed in detail in Section V, "Discussion and Interpretation of Results."

The theoretically calculated Chapman-Jouguet detonation equilibrium product composition, as mole fraction of specie present, are plotted as a function of initial pressure and various percent additive in Fig. 31 for the pure stoichiometric hydrogen-oxygen mixture (i. e., the "basic mixture") and the basic mixture admixed with helium or argon, and in Fig. 32 for the basic mixture admixed with carbon dioxide. The theoretical Chapman-Jouguet detonation and non-reactive

shock wave temperatures and density ratios, plotted as a function of initial pressure and percent additive, are presented in Fig. 33 for the basic mixture ( $2\text{H}_2 + \text{O}_2$ ) admixed with helium, in Fig. 36 for the argon-additive mixtures, and in Fig. 37 for the carbon dioxide-additive mixtures. The theoretically calculated Chapman-Jouguet detonation static pressure ratio ( $p''/p'$ ), the non-reactive shock wave static pressure ratio ( $P_{\text{NS}}/p'$ ) and impact pressure ratio ( $P_{\text{INS}}/p'$ ) as a function of initial pressure and percent additive are presented in Figs. 38 and 39 for the basic ( $2\text{H}_2 + \text{O}_2$ ) mixture without and with helium or argon additive, and in Fig. 40 and 41 for the carbon dioxide-additive mixtures. The calculated detonation wave impact pressure ratios were very close to the normal shock wave pressure ratios (see Tables 1 through 12, Appendix VIII) and were not plotted to avoid confusion. Presented in Fig. 42 are the theoretically calculated Chapman-Jouguet detonation velocity and static pressure ratio as a function of initial mixture pressure for the pure stoichiometric hydrogen-oxygen mixture.

#### B. Experimental Measurements of Detonation Velocities and Pressures

Experimental measurements were made to determine the detonation velocities and detonation static pressures, as a function of initial gas mixture pressure at one constant temperature ( $300^\circ\text{K}$ ), in stoichiometric hydrogen-oxygen mixtures admixed with helium,

argon or carbon dioxide. The detonation velocities and detonation static pressures were measured at exactly the same initial temperature and compositions of the stoichiometric hydrogen-oxygen-additive mixtures as those selected for computation of theoretical Chapman-Jouguet detonation and non-reactive shock parameters. The initial gas-mixture pressures for the experimental investigation, however, were limited to a range of  $1/2$  to 50 atmospheres for the velocity measurements and to a range of 1 to 5 atmospheres for the detonation static pressure measurements. The theoretical calculations covered a much wider range of initial gas-mixture pressures; i. e.,  $1/2$  to 1000 atmospheres. It should be noted, however, that experimental measurements of velocity were made at initial gas-mixture pressures of 1,  $2-1/2$ , 5, 10, 20, 30, 40, and 50 atmospheres, and of detonation static pressure at 1,  $2-1/2$  and 5 atmospheres initial pressure, whereas no theoretical calculations were made for initial pressures of  $2-1/2$ , 30, 40 and 50 atmospheres. Theoretical values of detonation velocity and pressure for these conditions, for use in comparing theoretical and experimental values, were obtained by graphical interpolation of the calculated velocity and pressure data (See Tables 13 through 24, Appendix VIII, and Figs. 35 through 41). Since the theoretical detonation velocities and pressures are well behaved, graphical functions of initial pressure, temperature and composition, very little uncertainty was introduced by this interpretation.

All detonation tests carried out in this investigation were conducted in a closed heavy-walled 1-1/2 inch inside diameter, 16-foot long stainless steel detonation tube, maintained at 300°K. Ignition was accomplished by means of an exploding wire ignitor located at one end of the detonation. Detection of the passage of the detonation wave front was accomplished by the use of flush-mounted ionization probes, located at four stations spaced 2-ft. apart along the detonation tube, in conjunction with precision electronic chronographs. Average wave velocities over the probe interval were calculated from the time required for the wave to pass between the two ionization probes and the measured distance between the centers of the probes. Steady velocity over the last two gage intervals was considered to be positive proof that a steady-state wave was propagating through the tube. Measurements of wave velocities were repeated a minimum of four times at the same initial conditions to check reproducibility.

For the majority of the experiments, it was possible to obtain stable detonation velocities of the various mixtures. For some mixtures and operating conditions, the detonation tube was found to be of insufficient length to permit achievement of the fully-developed stable Chapman-Jouguet detonation wave. For these mixtures, velocities were obtained of the wave propagation as it approached the fully-developed stable detonation condition. Where possible an

attempt was made to obtain a reasonable estimate of the stable detonation velocity by extrapolation of this data. Also, for some mixtures and operating conditions, it was not possible to establish a detonation; i. e., the detonation limits of pressure or concentration were exceeded, and the detonation did not occur or was quenched. In most of these latter mixtures, the ionization levels in the wave propagation were too low to trigger off the ionization probe sensors. These special cases will be considered in more detail in Section V, "Discussion and Interpretation of Results."

Detonation static pressures were determined through the use of a flush-mounted Kistler miniature (1/4-inch diameter) piezoelectric quartz crystal pressure transducer in conjunction with an electronic analog compensation device ("DATTA"), amplifier-calibrator and oscilloscope. (Refer to Appendices VI and VII for a detailed description of the experimental equipment, instrumentation and techniques used in this investigation.) Measurements of detonation static pressure (and wave velocities) were repeated three or more times at the same initial conditions to check reproducibility. Pressure measurements were made only for those mixtures where preliminary velocity measurements indicated that a fully-developed detonation wave had been achieved. The pressure measurements were limited to initial pressures to 5 atmospheres.

The average static detonation pressure was used for comparison with the theoretically calculated Chapman-Jouguet value. This was obtained from the oscillogram pressure-time traces by drawing a "best" bisector through the envelope formed by an irregular oscillations appearing on the record over the period of approximately 10 to 60 microseconds, where the pressure remains sensibly constant. This occurs in the region immediately following the reaction zone and before the rarefaction zone, or in the so-called "Chapman-Jouguet region."

Previous investigators (15, 48, 92, 120, 121, 182, 264) have determined that for detonable gaseous mixtures similar to those used in this investigation, initially at atmospheric pressure, the reaction time is less than 1 microsecond and the thickness of the wave is approximately 1 mm. Both the reaction time and wave thickness were found to decrease rapidly as the initial pressure increases. Thus, no attempt was made to determine pressures existing in the shock front (von Neumann "spike"), in the induction zone, or in the reaction zone of the wave, since it had been determined previously that these measurements were outside the limits of resolution obtainable with the present measuring system. This at best was on the order of 3 microseconds rise time.

All in all over 500 runs were carried out in four hydrogen-oxygen

mixtures, i. e. , stoichiometric hydrogen-oxygen mixtures pure and admixed with helium, argon or carbon dioxide. Over 100 conditions were investigated, encompassing a range of additive compositions from 0 to 50% by volume over a range of initial pressures from 1/2 to 50 atmospheres. The results of these runs are presented in Tables 13 through 24, Appendix IX and in Figs. 35 through 47. The maximum deviation of any individual velocity from the average in any one run, as well as the maximum experimental scatter between runs at the same initial conditions (i. e. , mixture, percent additive and initial pressure), was less than 1/2%, except for those runs at initial pressures and concentrations of additive where fully-developed steady-state detonation had not been achieved. The deviation of the individual velocities from the average in any one run is accountable to either experimental error or to actual fluxuations in the wave characteristics itself. With the method of velocity measurement used in these experiments it was not possible to determine if deviations were truly phenomonological or due to any inherent inaccuracies in the experimental techniques used. These special cases will be discussed in more detail in a later portion of this section. A comparison of experimental detonation rates and static pressures with those calculated by means of the Chapman-Jouguet theory is possible only when the observed measurements are those of the fully-developed steady-state detonation wave. Thus only the

steady-state fully-developed detonation velocities and static pressures determined experimentally were plotted in Figs. 35 through 47 for comparison with theoretical values.

#### 1. Stoichiometric Hydrogen-Oxygen Mixtures

In stoichiometric hydrogen-oxygen mixtures, measurements were made of detonation velocity at initial gas-mixture pressures of 1/2, 1, 2-1/2, 5, 10, 20, 30, 40 and 50 atmospheres; and measurements of detonation static pressure as well as detonation velocity were made at initial gas mixture pressures of 1, 2-1/2 and 5 atmospheres.

Table 13, Appendix IX, presents the results of the measurements of velocity and pressure in these mixtures. Included in this table are the following data for each test run: the average time of travel for the wave over each 2-foot probe interval (i. e., original experimental data), the average wave velocity over each 2-foot probe interval, the average experimental steady-state detonation velocity, the measured detonation static pressure, the theoretical Chapman-Jouguet detonation and static pressure, the deviations of the measured from the theoretically calculated ideal Chapman-Jouguet detonation velocity and pressure, and the average experimental steady-state detonation velocity, static pressure and deviations based on the average of all the runs at each initial condition. Fig. 43 is a representative plot of the original experimental data; i. e., the average time of wave propagation (  $\Delta t$  ) over each 2-foot probe interval as a function of



the distance of the wave travel from the igniter end for each initial pressure. The points plotted are located in the graph half-way between the probe interval considered. The straight lines joining the points are not intended to have physical meaning. This composite chart shows pictorially the influence of initial pressure on the detonation velocity in stoichiometric hydrogen-oxygen mixtures.

No difficulty was encountered in obtaining experimentally consistent and reproducible detonation velocity data for the stoichiometric hydrogen-oxygen mixtures at all initial pressures investigated. Even at initial pressures of  $1/2$  atmosphere, with the exception of the first probe interval where the detonation wave apparently had not yet fully stabilized (See Fig. 43 and Table 13, Appendix IX), the results are quite consistent and reproducible.

In Fig. 44 a, b, and c are presented typical oscillogram pressure-time records of the detonation static pressure in stoichiometric hydrogen-oxygen mixtures at initial gas-mixture pressures of 1,  $2\frac{1}{2}$ , and 5 atmospheres, respectively. The average experimental steady-state detonation velocities, along with the theoretical Chapman-Jouguet detonation velocities, for the stoichiometric hydrogen-oxygen mixtures (0% additive lines) are presented as a function of initial gas-mixture pressure in Figs. 35, 36, 37 and 42. The

average experimental detonation static pressure to initial pressure ratios as a function of initial pressure, together with the theoretical Chapman-Jouguet detonation static pressure ratios for this mixture (0% additive) are given in Figs. 38 through 42. Also included in Fig. 42 are experimental values of detonation velocity and detonation static pressure over the limited ranges of initial pressure reported by other investigators for the stoichiometric hydrogen-oxygen mixture (See Table 25, Appendix X). Each experimental point representing data obtained in this investigation is an average of the values obtained from a minimum of four tests for velocity and three for pressure.

## 2. Stoichiometric Hydrogen-Oxygen-Helium Mixtures

Four mixtures were used at initial gas-mixture pressures of 1/2, 1, 2-1/2, 5, 10, 20, 30, and 50 atmospheres to determine the effect of helium upon the detonation velocity in a stoichiometric mixture of hydrogen and oxygen. These four mixtures were the following:

- |   |              |
|---|--------------|
| (2H <sub>2</sub> + O <sub>2</sub> )+ 1/3 He | (10% He)     |
| (2H <sub>2</sub> + O <sub>2</sub> )+ He     | (25% He)     |
| (2H <sub>2</sub> + O <sub>2</sub> )+ 1.8 He | (37-1/2% He) |
| (2H <sub>2</sub> + O <sub>2</sub> )+ 3 He   | (50% He)     |

The detonation static pressures as well as the detonation velocity was measured in the 10% and 25% helium-additive mixtures at initial gas-mixture pressures of 1 and 5 atmospheres. In the 37-1/2%

additive mixtures the detonation static pressures were measured at 2-1/2 and 5 atmospheres, and in the 50% helium-additive mixtures at 5 atmospheres only. This was because preliminary velocity measurements had indicated that stable detonation had not been achieved in these mixtures at any lower initial pressures in the 16-foot length - 1-1/2 inch I. D. detonation tube. The mixture burned and the spatial velocity increased towards the downstream end of the tube, but the propagation rates were still unsteady and below those of a steady detonation wave. A fully-established detonation wave could have been established if the tube were longer. (Steady-state fully-developed detonation waves only were of prime concern in this investigation). This can be observed most easily by inspection of the composite chart of wave propagation times between probe intervals ( $\Delta t$ ) (Fig. IV-15) and from the values of the non-stabilized wave propagation times ( $\Delta t$ 's) and velocities for these two mixtures at any lower initial pressures (Tables 16 and 17, Appendix IX). It is pointed out further that no detonation could be established in the 50% helium-additive mixtures at 1/2 atmosphere initial pressure; i. e., outside the detonation limits. The ion probe detectors were not sensitive enough to detect passage of the wave, although combustion was verified by audio means and by measurement of the pressure in the tube after completion of each test. These special cases will be discussed in more detail in Section V, "Discussion and Interpretation of Data."

The results of the measurements of wave propagation time between probe intervals ( $\Delta t$ ), wave velocity, and detonation static pressure in these mixtures are presented in Tables 14 through 17, Appendix IX. Fig. 45 is a composite chart of the "average time of wave propagation" ( $\Delta t$ ) over each 2-foot probe interval (original experimental data), as a function of the wave travel from the igniter and for each initial gas-mixture pressure and each hydrogen-oxygen-helium mixture investigated. In Fig. 44 l and m are presented typical oscillogram pressure-time records of the detonation static pressures in stoichiometric hydrogen-oxygen mixtures admixed with 10% helium by volume at initial pressures of 1 and 5 atmospheres, respectively; in Fig. 44 n and o for 25% helium-additive mixtures at 1 and 5 atmospheres initial pressure, respectively; in Fig. 44 p and q for 37-1/2% helium-additive mixtures at 2-1/2 and 5 atmospheres initial pressure, respectively; and in Fig. IV-44 r for 50% helium-additive mixture at 5 atmospheres initial pressure. In fig. 35 the average experimental steady-state detonation velocity, together with the theoretical Chapman-Jouguet detonation velocities for all the helium-additive mixtures investigated, are plotted as a function of initial gas-mixture pressure. Also included in Fig. 35 are experimental values of detonation velocity over the limited range of initial pressure and percent additive reported by other investigators for the stoichiometric hydrogen-oxygen-helium mixtures. (See also Table 25, Appendix X).

Some of the literature values of experimental velocity presented in Table 25, Appendix X at casual glance might appear to overlap some of the work accomplished in this investigation. This inference would be incorrect. It is pointed out that the experimental data reported by other investigators in many instances were obtained from tests carried out using compositions of helium added to the basic ( $2\text{H}_2 + \text{O}_2$ ) mixture which were different than those used in the present investigation. To permit direct comparison with the results obtained in this investigation, the reported values of detonation velocity, in these particular cases, were plotted as a function of percent additive (helium) in the stoichiometric hydrogen-oxygen mixture. The values of detonation velocity at the percent additive identical to those investigated in this study then were obtained by interpolation. It is these interpolated data, in addition to the relatively small amount of "originally" reported data, which are presented in Table 25, Appendix X of this dissertation. As will be seen when the other additive mixtures are discussed, the same type of procedure was used to obtain literature values of detonation velocity for the argon-additive and carbon dioxide-additive mixtures to be used for direct comparison with the values obtained in this investigation.

It should be indicated also that the experimental detonation velocity data reported by Bollinger, et. al. (21, 22, 23, 25, 26) were obtained as a by-product of their research on detonation induction

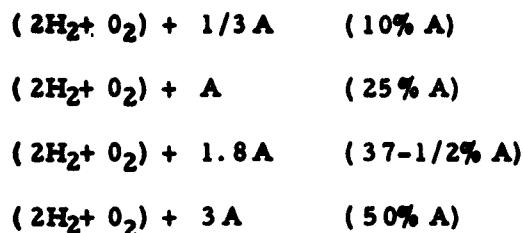
distances. They made no claim for the accuracy of these results. For this reason, the original experimental data for the helium-additive mixtures reported by Bollinger, et. al., i. e., induction distance vs. wave propagation rates, were replotted. Then by careful extrapolation a redetermination was made of the wave propagation rate when steady-state conditions would be obtained; i. e., the steady-state detonation wave velocity. It is these "redetermined" values of detonation velocity which are presented in Table 25, Appendix X. These revised steady-state detonation velocity values were also used to obtain the graphically interpolated values of detonation velocity at specific percentages of helium. These appear in Fig. 35 and in Table 25, Appendix X and are indicated as being accountable to this particular reference (25, 26).

The average experimental detonation static pressure ratios along with the theoretical Chapman-Jouguet detonation static pressure ratios are plotted as a function of initial gas-mixture pressure and percent additive in Figs. 38 and 39 for these mixtures. (It should be noted that the same plot can be used to represent the theoretical state properties of either the helium-or argon-additive mixtures).

### 3. Stoichiometric Hydrogen-Oxygen-Argon Mixtures

The following four gas mixtures were employed at initial gas-mixture pressures of 1/2, 1, 2-1/2, 5, 10, 20, 30 and 50 atmospheres

to determine the detonation velocity in stoichiometric hydrogen-oxygen-argon mixtures:



The detonation static pressure and detonation velocity were measured in the 10%, 25% and 37-1/2% argon-additive mixtures at initial gas-mixture pressures of 1 and 5 atmospheres, and in the 50% argon-additive mixtures at 2-1/2 and 5 atmospheres initial pressure.

As in some of the helium-additive mixtures, it was found from preliminary velocity measurements that in the 50% argon-additive mixture at 1 atmosphere initial pressure (See Fig. 46 and Table 21, Appendix IX) a fully-developed detonation wave had not been achieved in the length of tube available. Thus pressure measurements were not made at this initial pressure for this particular mixture. The results of the measurements of wave propagation times ( $\Delta t$ 's) between probe intervals, wave velocity and detonation static pressure in these mixtures are presented in Tables 18 through 21, Appendix IX. Fig. 46 is a composite chart of the experimentally measured "average time of wave propagation" ( $\Delta t$ ) between probe intervals as a function of the distance of the wave travel from the igniter end for each initial gas-mixture pressure and each hydrogen-oxygen-argon mix-

ture investigated.

In Fig. 44 d and e are shown typical oscillogram pressure-time records of the detonation static pressure in stoichiometric hydrogen-oxygen mixtures admixed with 10% argon by volume at initial pressures of 1 and 5 atmospheres, respectively; in Fig. 44 f and g for 25% argon-additive mixtures at 1 and 5 atmospheres, respectively; in Fig. 44 h and i for 37-1/2% argon-additive mixtures at 1 and 5 atmospheres, respectively; and for 50% argon-additive mixtures at 2-1/2 and 5 atmospheres initial pressure, respectively. The average experimental steady-state detonation velocities, as well as the theoretical Chapman-Jouguet detonation velocities for all the argon-additive mixtures investigated, are given as a function of initial gas-mixture pressure in Fig. 36. Also included in Fig. 36 are experimental values of detonation velocity over the limited range of initial pressures and percent additive reported by other investigators for the stoichiometric hydrogen-oxygen-argon mixtures. (See also Table 25, Appendix X).

Again, as with the reported values of detonation velocity for the helium-additive mixtures, to permit direct comparison with the results obtained in this investigation, many of the literature values of detonation velocity plotted in Fig. 36, and presented in Table 25, Appendix X, were obtained by interpolation of the graphs of the originally reported literature values of detonation velocity, plotted as a



function of percent additive. In addition, as with the helium-additive mixtures, the detonation velocity data accountable to Bollinger, et. al, (25, 26) was obtained by re-evaluation of their original experimental induction distance data to obtain a stable Chapman-Jouguet detonation velocity for the basic ( $2\text{H}_2 + \text{O}_2$ ) mixtures containing the same ammounts of argon as those tested in this investigation.

The average experimental detonation static pressure ratios along with the theoretical detonation pressure ratios, as a function of initial pressure and percent additive are presented in Figs. 38 and 39 for these mixtures.

#### 4. Stoichiometric Hydrogen-Oxygen-Carbon Dioxide Mixtures

The following four mixtures were used at initial gas-mixture pressures of 1/2, 1, 2-1/2, 5, 10, 20, 30 and 40 atmospheres to determine the influence of carbon-dioxide on the detonation velocity in a stoichiometric hydrogen-oxygen mixture:

$(2\text{H}_2 + \text{O}_2) + 1/8 \text{ CO}_2$	(4% $\text{CO}_2$ )
$(2\text{H}_2 + \text{O}_2) + 1/3 \text{ CO}_2$	(10% $\text{CO}_2$ )
$(2\text{H}_2 + \text{O}_2) + \text{CO}_2$	(25% $\text{CO}_2$ )
$(2\text{H}_2 + \text{O}_2) + 3 \text{ CO}_2$	(50% $\text{CO}_2$ )

The detonation static pressure and the detonation velocity were measured in the 4% by volume carbon dioxide-additive mixtures at initial gas-mixture pressures of 1 and 5 atmospheres. In the 25% carbon dioxide-

additive mixtures these measurements were made at 5 atmosphere initial pressure only since preliminary velocity measurements indicated that stable detonation had not been achieved in the length of the detonation tube used for this mixture at lower initial pressures. (See Table 24, Appendix IX and Fig. 47). Attempts were made to determine the detonation velocity in 50% carbon dioxide-additive mixtures. It was not found possible to establish a detonation in this system at initial pressures up to 40 atmospheres. In fact even ignition of the mixture was difficult. The ion probe detectors, as in some helium-additive mixtures investigated, were not sensitive enough to detect passage of a wave in this system, therefore no velocity data was obtained. However, combustion in this system was verified by audio observation and by observation of the pressure in the detonation tube after each test was completed. (These same characteristics were encountered in the 25% carbon dioxide-additive mixtures at 1/2 atmosphere initial pressure). No theoretical calculations of the 50% carbon dioxide-additive mixture were made since no experimental velocities or pressures were obtained in this system. The results of the measurements of wave propagation times ( $\Delta t$ 's) wave velocity and detonation static pressure in these mixtures are presented in Tables 22 through 24, Appendix IX. Fig. 47 is a composite chart of the experimentally measured "average time of wave propagation" ( $\Delta t$ ) between probe intervals as a function of the distance of the wave travel from the igniter end for each initial gas-mixture pres-

sure and each carbon dioxide-additive mixture investigated. In Fig. 44 s and t are shown typical oscillograms pressure-time records of the detonation static pressure in stoichiometric hydrogen-oxygen mixtures admixed with 4% by volume carbon dioxide at initial gas-mixture pressure of 1 and 5 atmospheres, respectively; in Fig. 44 u and v for 10% carbon dioxide-additive mixtures at 1 and 5 atmospheres, respectively; and in Fig. 44 w for 25 % carbon dioxide-additive mixtures at 5 atmospheres initial gas-mixture pressure. The average experimental steady-state detonation velocities together with the theoretical Chapman-Jouguet detonation velocities for the carbon dioxide-additive mixtures are plotted as a function of initial gas-mixture pressure in Fig. 37. Also included in Fig. 37 are experimental values of detonation velocity, over a limited range of initial pressures and percent additive, reported by Bollinger, Fong and Edse (25, 26) for the stoichiometric hydrogen-oxygen-carbon dioxide mixtures. (See also Table 25, Appendix X). To the knowledge of this investigator as part of this dissertation are the only research efforts reported pertaining to the effect of carbon dioxide on the mechanism, formation and/or propagation of detonation in hydrogen-oxygen mixtures. As indicated previously, Bollinger, et. al. (25, 26) were interested primarily in predetonation phenomena; and their reported values of detonation velocity admittedly were not of the highest accuracy. For this reason, as with the helium-additive and argon-

additive mixtures, the original test data of Bollinger, et. al, was replotted and re-evaluated to obtain a more quantitative estimate of the stable detonation velocity. Then these revised values were graphically interpolated to obtain values of detonation velocity for stoichiometric hydrogen-oxygen mixtures containing the same percentage additive as those mixtures tested in this investigation. It is these "re-evaluated" and "interpolated" values of detonation velocity, accountable to Bollinger, et. al., which are presented in Table 25, Appendix X. These are the values which are plotted and compared to the results obtained in this investigation in Fig. 37. The average experimental detonation static pressure ratios together with the theoretical Chapman-Jouguet detonation static pressure ratios as a function of initial pressure and percent additive are presented in Figs. 40 and 41 for these mixtures.

## V DISCUSSION AND INTERPRETATION OF RESULTS

This section will be concerned primarily with the discussion and interpretation of the theoretical calculated Chapman-Jouguet detonation and non-reacting normal shock wave parameters and experimentally determined steady-state detonation velocities and static pressures for the stoichiometric hydrogen-oxygen-additive mixtures considered in this investigation. Included will be a discussion of the precision and reliability of the experimental measurements and theoretical calculations, and a comparison between theoretical detonation parameters. In particular, a comparison will be made between theoretical and experimental values of detonation velocity and static pressure for each system investigated as influenced by initial gas-mixture pressure and percent additive. Also presented will be comments pertaining to the use of either the "frozen" or "equilibrium" speed of sound in the calculation of detonation parameters. Finally, a discussion will be made of the data obtained on detonation wave build-up and stabilization; i. e., the predetonation or detonation induction region. The theoretical and experimental aspects of each system, in general, will first be treated separately. Then pertinent comments pertaining to all systems will be made.

### A. Accuracy and Reliability of Measurements and Theoretical Calculations

### 1. General Discussion of Pressure Measurements

As can be seen by examination of the pressure-time traces obtained for each mixture investigated (Fig. 44), low frequency oscillations, sometimes quite high in amplitude, superimposed on or modulated the output signal from the pressure transducer. These spurious signals are not believed by this investigator to be caused by or to represent the true phenomenological events occurring in the detonation wave. Some of this "noise" may be due to the high gain of the electronic equipment used. However, rather it is believed that these perturbations are caused mainly by "ground waves" traveling through the metal detonation tube walls ahead of the shock wave in the gas upon formation of the detonation wave and imparting a longitudinal acceleration to the pressure transducer.

Preliminary pressure measurements were obtained in this investigation of shock waves and of stoichiometric hydrogen-oxygen detonations at 1 atmosphere initial pressure, utilizing a rigid-type pressure transducer mount. The results obtained indicated that in all probability the effect of "ground waves" on the pressure transducer thus mounted would not seriously affect the interpretation of the dynamic pressure oscilloscope traces (Refer to Appendix VI-E and Section V-A1). While these superimposed oscillations did not prevent the obtaining of fairly good mean values of the pressure signals, they did limit the precision of the measurements.

Other factors which may have affected the precision of the pressure measurements include the differences in static and dynamic calibration determinations of the pressure transducer. Some small discrepancies are present due to the interaction of the pick-up with a shock wave which undoubtedly causes some differences from static conditions. However, it is felt by this investigator that these differences are small because of the small mass and inertia effects of the pick-up (See Appendix VI-E). Also, it is felt that any errors due to these discrepancies are negligible relative to the uncertainty associated with the values of the mean detonation static pressures obtained in this investigation.

Thus, due to the uncertainties involved in the interpretation of the oscilloscope traces and to the possible errors caused by the factors discussed above, it is felt that the average detonation static pressures reported in this investigation (See Tables 13 through 24, Appendix IX) cannot be relied upon to more than  $\pm 20$  psi in the lower pressure range (up to 500 psi),  $\pm 40$  psi in the middle range (up to 1000 psi), and  $\pm 60$  psi in the highest pressure range measured (up to 1500 psi).

Inspection of the data presented in Tables 13 through 24, Appendix IX, reveals also that the difference between the theoretical Chapman-Jouguet detonation static pressure and measured detonation

static pressure in a large number of cases is quite close to or less than the experimental uncertainty associated with the value of measured pressure; i. e. , the deviations between theoretical and experimental detonation static pressure values fall within the range of experimental error associated with the pressure measuring system. It can be seen, therefore, that the pressure measurements obtained in this investigation are not sufficiently precise to permit quantitative evaluation of the influence of additives on the absolute magnitude of the detonation parameters or on the mechanism of detonation in gaseous mixtures.

Due to the extraneous oscillations superimposed on the signal output from the pressure transducer ( see Fig. 44), it also was not possible to determine unequivocally the rate of the slowly decreasing pressure in the trailing position of any of the pressure-time oscilloscope traces obtained. If this could have been ascertained it may have been possible to have drawn some conclusions pertaining to the possibility of some of the chemical reactions continuing in the rarefaction wave following the termination of the effective Chapman-Jouguet plane. In a few instances, it appeared that such could have been done ( see Fig. 44, a, j, m, n, and p). However, it is felt that even in these cases, evidence is not sufficient to warrant a quantitative interpretation. No quantitative conclusions can be made on the basis of the rather qualitative pressure measurements obtained,



notwithstanding the quite precise velocity measurements obtained, pertaining to the achievement of chemical equilibrium in any of the mixtures investigated over the range of initial pressures considered; i. e. , up to 5 atmospheres.

Although the precision of the pressure measurements appears to be somewhat limited, the average detonation static pressures measured and reported in this investigation are felt to be reasonably reliable measurements of the static pressure in the steady-state Chapman-Jouguet region in the steady detonation wave. Even though they are not quantitatively precise, it is felt too that the measurements are of the correct magnitude. Also they are certainly sufficiently accurate to permit qualitative conclusions to be made pertaining to the magnitudes and trend of the detonation static pressure or the ratio of the detonation static to initial pressure with initial pressure for the various mixtures investigated over the range of initial pressures considered. For example, it can be seen ( Figs. 38 through 42 and Tables 13 through 24, Appendix IX) that in all cases the pressure measured was of the same order of magnitude, was not too far away from, and followed the same trend with initial pressure as the ideal Chapman-Jouguet detonation static pressures. Also the averages of the mean detonation static pressures appear to follow the same trend as the experimental detonation velocity measurements; i. e. , the measured pressure appears to be lower than the theoretical Chapman-

Jouguet pressure at the lower initial pressures. These points will be covered in more specific detail in subsequent portions of this section when the theoretical and measured values of detonation static pressure for the various mixtures of interest in this investigation are discussed and compared.

In addition to the observations discussed above, no indication was found of either a sharp pressure peak, the so-called "von Neumann spike," or an induction zone immediately following the "spike" (See Fig. 29) on any of the pressure-times oscillograms for any of the mixtures at any of the initial pressure conditions investigated. (See Fig. 44). As indicated before (See Sections IIE, page 36 and IV-B, page 91 for details) previous investigators have shown that response times comparable to a few mean free paths are required for detection of a shock front and response times of a fraction of a microsecond are required for the reaction zone in detonable gaseous mixtures comparable to those investigated at 1 atmosphere initial pressure. Also it was determined that the response time required decreased as the initial pressure increased. Results obtained during the preliminary check-out tests of the pressure measuring system indicated that the pressure measuring system, which had to be operated below its maximum capabilities due to pressure sensor mounting and electronic difficulties, was incapable of detecting and measuring transients which had response times less

than approximately 3 microseconds. Thus, it was to be expected that no indication of the "von Neumann spike," the induction zone or the reaction zone would be seen on the pressure-time oscillograms, since these measurements are outside the limits of resolution obtainable with the present pressure sensor and associated electronics. (See Appendix VI-E for complete details of the pressure measuring system, capabilities and limitations).

It is apparent then that on the basis of the pressure traces obtained in this investigation no quantitative conclusions can be made pertaining either to the existence or non-existence of the "von Neumann spike" or to an induction zone immediately following the "spike." Also no quantitative conclusions can be made pertaining to the true model of the detonation wave structure. Actually it is not too unreasonable to postulate that all the modern models of the detonation wave structure may be correct, with one model conforming more closely to the real situation than another over a limited range of pressures, temperatures and compositions. For example, it is entirely possible that the Hershfelder, et. al. (72, 153, 154, 156) model, the Cook "heat pulse model" (57, 64, 65), or the Fay two-dimensional model (118, 119, 120, 122) may be more applicable at low initial pressures and/or for very dilute mixtures, where transport mechanisms within the wave itself may be important and where there may be intimate coupling between the shock wave and

the burning region. On the other hand, the modified NDZ model postulated in this investigation, which assumes zero transport effects, may become more realistic as the initial pressure increases and the reaction zone width decreases. It will require additional intensive theoretical and experimental investigation, including the use of very accurate and highly responsive instrumentation, before it can be determined quantitatively which structural model best describes the microscopic features of the stable detonation wave in the real situation. It should be noted that all the modern models of the detonation wave structure stipulate the Chapman-Jouguet condition at the completion of the reaction zone. Thus the assumption of any particular structural model of detonation does not influence the theoretical calculation of the macroscopic properties of the stable fully-developed detonation wave.

As can be readily inferred from the above discussion, much of the indecision pertaining to the quantitative interpretation of the mechanism of detonation (and also possibly the detonation structure) as influenced by additives in this investigation is primarily due to some of the unfavorable characteristics of the pressure measuring system. As pointed out previously, the pressure measuring system was operated, by necessity, considerably below its maximum capabilities because of difficulties arising from the pressure sensor mounting as well as to difficulties in the electronic circuitry. These

difficulties, although recognizable and not insurmountable, would have involved additional design, development, fabrication and testing work for their satisfactory solution. In view of the relatively large research effort already encompassed by this investigation and the great amount of time already expended, but primarily due to the limitation on the available laboratory facility time remaining, these difficulties could not be eliminated.

The full capabilities of the pressure measuring system and technique utilized in this investigation could be attained with a reasonable amount of additional work. Of primary importance would be the elimination of the extraneous oscillations or "ground waves" due to the type of pressure transducer mounting arrangement used. Use of a shock-mounted arrangement similar to that described previously ( Appendix VI-E3 ) would eliminate this problem. Use of and strict inspection to insure maintaining of smooth clean tube walls would remove any additional "noise" due to shock reflections on any surface irregularities.

Also the upper limit of response capabilities of the pressure measuring system could be attained if the random noise, due primarily to thermionic disturbances in the electrometer tube of the amplifier-calibrator, were eliminated. This would remove the necessity for using the low-pass 150 KC output filter in the DATTA

input circuitry (See Appendix VI-E-4). This could be accomplished by using a different type of electrometer tube and/or by confining the electrometer tube in a low humidity, very low temperature, controlled environment, possibly by cryogenic means. The rise time for the entire pressure measuring system under these improved conditions would be on the order of 0.5 microseconds, in comparison to the approximately 3 microseconds response time capabilities of the pressure sensing equipment as used in this investigation.

In addition, the limitations on initial pressure could be removed by incorporation of a high-response pressure transducer with the required specifications but better capable of withstanding the rugged environment associated with the detonation phenomena. (See Appendix VI-E-2) than that used in the present investigation. Finally, the uncertainty in the measured values could be reduced to a minimum if the pressure transducer and associated electronics were calibrated dynamically throughout the entire range of operation.

With the pressure measuring system then capable of operating at its optimum capabilities, quantitative determination could be made of the Chapman-Jouguet pressure. These values together with simultaneously measured values of detonation velocity would assist materially in the analysis and interpretation of the mechanism of detonation in gaseous mixtures. This would include the interpretation of

deviations between experimental and theoretical values of detonation parameters. In addition the apparatus and technique would be suited to the study of the internal wave structure, including high temperature and high pressure kinetic studies in the reaction zone. Possibly it could assist in the determination of which sound speed is most correct to use in the calculation of Chapman-Jouguet detonation parameters, the "frozen" or the "equilibrium." However, in all probability, the response still would not be rapid enough to sense the very steep shock front; i. e., "von Neumann spike," or the induction zone.

It should be pointed out in summary that in the opinion of this investigator, the improved version of the pressure measuring instrumentation and technique has capabilities of being an excellent research tool and would be of great utility to scientists working the fields of detonation and shock wave propagation. Also it would be valuable to those working in the areas of high pressure and high temperature kinetics, including relaxation phenomena, and in other research areas where there is a need for precise, very high response pressure measurements.

## 2. General Discussion of Detonation Velocity Measurements.

The accuracy associated with the measured values of detonation wave propagation, presented in Tables 12 through 24, Appendix IX,

is considerably greater and the probable error considerably less than that associated with the measured values of detonation static pressure. The guaranteed accuracy of time measurement with the electronic chronograph used in this investigation (See Appendix VI-D3) is 0.0002% of the total elapsed time interval measured  $\pm$  0.1 microsecond. Elapsed time intervals measured in this investigation ranged from about 150 to 350 microseconds over a two-foot probe interval; i. e., average velocities of steady detonation waves ranging from about 2000 to 4500 meters per second. Thus the maximum error introduced by the counting system is less than one-tenth of one-percent between adjacent probes and less than two-hundredths of one percent over the thirteen-foot test section. This does not include any errors which may be introduced at the ionization probes. For example, probe errors can occur if the time needed to form the conducting path on each probe is different. However, this error is believed to be small compared to the elapsed time period measured in the experiments. To minimize this error, particular attention was paid to maintaining close tolerances, similar fabrication and assembly techniques and proper positioning of the probes in the detonation tube. This accuracy also does not include errors introduced by possible variation in other experimental variables such as initial temperature, pressure and composition and mixture uniformity. Considerable effort was taken to minimize such variations.



### 3. Influence of Errors in Thermodynamic Properties on the Theoretical Chapman-Jouguet Detonation Parameters

The basic thermodynamic data used in improvising the tables of thermodynamic functions used in the computation of the theoretical Chapman-Jouguet detonation and normal shock wave parameters in this investigation (See Appendix IV) were obtained from the latest and most reliable literature sources available (7, 13, 54, 130, 131, 144, 152, 228, 271, 277, 286). Errors in the thermodynamic functions are quite small, especially for the monatomic and many of the diatomic gaseous species. The uncertainties increase as the sensitivity of the thermodynamic functions to changes in the spectroscopic constants increase in the order: free energy, enthalpy, entropy and specific heat. In most cases, the thermodynamic properties of the dominant species in the products of detonation formed from the elements carbon, hydrogen, and oxygen (which are the only elements of concern in this investigation) are very well defined and are quite reliable. For example, Gordon (130) and Hilsenrath, et. al. (152) summarize the estimated accuracy of the entropy data over the temperature range of 3 000° to 5 000° K. as follows:

Monatomic gases	0.002% - 0.004%
CO, H <sub>2</sub> , OH	0.008% - 0.01%
CO <sub>2</sub> , H <sub>2</sub> O	0.020 - 0.06%
triatomic gases, CH	0.04%

The error is about proportional to the square of the absolute temperature. In addition, data calculated from Hilsenrath, et. al. (152) indicates that the uncertainties in the theoretical values of the free energy, enthalpy, and specific heat are of approximately the same order of magnitude. The specific heats have the greatest uncertainty, but the uncertainty is still well under 1/2% for the temperature range of 3 000° to 5 000° K.

The reliability of some of the equilibrium constant values is much less than that of the thermodynamic functions. This is especially so for the free radical equilibria where the dissociation energies or heats of formation are quite uncertain. For example, the uncertainty in  $\ln_e K_p$  for CH, CH<sub>2</sub>, CH<sub>3</sub>, and CHO radicals is at least 10% (130). However, these radicals, as well as the molecules such as C<sub>2</sub>, C<sub>3</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>OH, C<sub>3</sub>, O<sub>3</sub>, and COH<sub>2</sub> are present in very negligible amounts in the detonation products of the mixtures of concern in this investigation (See Tables 1 through 12, Appendix VIII.) Thus, any uncertainty in their thermodynamic properties or equilibrium constants is relatively insignificant insofar as their effect on the values of the calculated detonation parameters is concerned.

The uncertainties in the equilibrium constants for the major

species involved in the detonation reaction products (i. e.,  $H_2O$ ,  $H_2$ ,  $O_2$ ,  $OH$ ,  $CO_2$  and  $CO$ ) are considerably smaller because of the greater reliability of the heat-of-formation and dissociation energy data. For example, from the data reported by Peek and Thrap (248, 249), the experimental uncertainties in the heats of formation for atomic oxygen was determined to be about 0.02%; for carbon monoxide, about 0.1%; for carbon dioxide, about .01%; and for gaseous carbon, about 0.3 %. Due to cumulative effects of these small uncertainties in the thermodynamic properties, including the heats of formation and the equilibrium constants for the species involved in the detonation products and reactants, there is undoubtedly a statistical uncertainty in the calculated detonation velocities, pressures and other parameters. It would be difficult to determine the precise magnitude of the resulting uncertainty. However, it is felt that the total uncertainty in the detonation velocities and other detonation parameters due to these uncertainties is very small in comparison to the possible deviations due to other effects. These effects will be discussed in subsequent portions of this section.

#### **B. Theoretical and Experimental Detonation Data**

From an examination of the theoretically calculated Chapman-Jouguet detonation product equilibrium specie concentrations, an insight can be obtained as to the chemical origins of the energy re-

leased by equilibrium detonations. Also determination may be made of the influence of additives and changes in initial state parameters, such as initial gas-mixture pressure, on the energy release, and therefore on the thermodynamic and aerothermodynamic properties of the detonation wave.

### 1. Stoichiometric Hydrogen-Oxygen Mixtures

The results of the theoretical calculations show (Fig. 31 and 32, 0% additive curves, and Table 1 - Appendix VIII) that the theoretical detonation equilibrium product for pure stoichiometric hydrogen-oxygen mixtures consists mostly of  $H_2O$ ; i. e., approximately 50% by volume at 1 atmosphere initial pressure. Also present are relatively smaller amounts of  $H_2$ ,  $H$ ,  $OH$ ,  $O_2$ , and  $O$ . The concentration and energy contributions of other constituents such as  $O_3$  were found negligible; i. e., mole fraction less than  $10^{-6}$ . These were not included in the plot. (The negligible effect of these minor constituents was suspected initially and conclusively proven by these calculations.) It is seen that as the initial pressure increases, the concentration of the  $H_2O$  continuously increases (i. e., approximately 50%  $H_2O$  at 1 atmosphere to 75% at 1000 atmospheres). Conversely the concentration of the other major components decrease, the dissociative products  $H$  and  $O$  exhibiting the greatest rate of decrease.

The change in specie concentration with increase in initial pressure ( Fig. 31 and 32) is as expected since an increase in initial pressure should cause a decrease in the dissociation process ( endothermic processes). An increase in reaction rates due to an increase in temperature in the shock front is also caused by an increase in initial pressure in actual detonations. This latter effect will be discussed in more detail subsequently in this section when the experimental results of this investigation are analyzed. The major end product of hydrogen-oxygen detonations that is responsible for their exothermic characters, i. e., energy supporting the wave propagation, is the formation of  $H_2O$ . The association effect of pressure on the detonation products thus would be expected to increase the energy available to support the detonation propagation. This is due to the reduction in dissociation of the species in the detonation products, which through their exothermic heats of formation contribute the majority of this energy. The detonation temperature, velocity, pressure and density are directly dependent upon the amount of energy released in the combustion. Thus, by the same token, for a given mixture an increase in initial pressure would be expected to yield an increase in these parameters. The theoretical calculations carried out ( Tables 1 through 12 - Appendix VIII) and the data plotted from these calculations ( Figs. 32 through 47) substantiate this contention. More will be said pertaining to the pressure effect and to the "available energy" increase later in this

section when experimental results of this investigation are analyzed (See Section V-E).

Figs. 33 and 34 and Table 1-Appendix VIII show that in the pure stoichiometric hydrogen-oxygen mixture, the theoretical detonation temperature and normal shock wave temperature increase, (approximately a 400°K temperature rise over an increase of 1000 atmosphere initial pressure or 10% in  $T'$  and 20% in  $T_{NS}$ ) the ratio of detonation density to initial density ( $\rho''/\rho'$ ) decreases and the ratio of normal shock wave density to initial density ( $\rho_{NS}/\rho'$ ) increases, as the initial gas-mixture pressure increases. It can be seen also (Fig. 33) that the temperatures in the normal shock zone are almost one-half the detonation temperatures, whereas the densities behind the normal shock wave are about twice the densities of the detonation wave. This is in conformity with values predictable from the fundamental thermodynamic equations.

The theoretically calculated Chapman-Jouguet detonation velocities for the stoichiometric hydrogen-oxygen mixtures also follow the expected trend with initial pressure as is evident by inspection of Figs. 35, 36, and 37 (0%-additive curves) and 42. The theoretical detonation velocities increase at a decreasing rate as the initial pressure increases. However, the influence of initial pressure is seen to be quite small. The change of velocity with change in initial

pressure, is approximately 330 meters for a change of 1000 atmospheres. The maximum possible theoretical velocity would be attained when no dissociation of the product gases occurred. Under these conditions, no chemical energy is involved in dissociating the products. This state of the product gases would occur if the pressure were infinite since an increase in pressure causes a decrease in the amount of dissociation. A velocity asymptote should be expected on the theoretically calculated velocity curves which the velocity would approach as the pressure increases towards infinity. This appears to be the case for the calculated Chapman-Jouguet detonation velocity curves, based on ideal properties of the product gases, not only for the stoichiometric hydrogen-oxygen mixtures, but for all mixtures considered in this investigation. (See Figs. 35, 36, and 37). Theoretical calculations of Chapman-Jouguet detonation and shock parameters for stoichiometric hydrogen-oxygen mixtures made in this investigation (including values of compositions, temperature, density, velocity, pressure, etc.) are in quite good agreement with those of other investigators (17, 24, 103, 105, 126, 134, 225, 264, 323). Any small deviations can be attributed to the following: (1) the use of slightly different thermodynamic data; (2) corrections of the initial mixture for non-ideality; (3) the use of a slightly different ambient temperature; (4) the use of either the "frozen" or "equilibrium" sound speed in the relationship for the Chapman-Jouguet condition ( $D = u'' + a''$ , or  $M'' = 1$ ) to determine the Chapman-Jouguet

point. This is opposed to the use of the slope of the Rayleigh line drawn from the initial state, tangent to the equilibrium Hugoniot curve as was done in this investigation to determine this point;

i. e.,

$$\left[ \frac{dp''}{d(1/\rho'')} \right]_{C-J} = - \left[ \frac{p'' - p'}{(1/\rho') - (1/\rho'')} \right]$$

A discussion pertaining to which speed of sound, the "frozen" or the equilibrium, " is the correct one to use in theoretically predicting detonation parameters, is given in a subsequent portion of this section (See Section V-C.)

From Fig. 42 it is seen that the experimental detonation velocity data obtained for the stoichiometric hydrogen-oxygen mixture in this investigation is on the whole in good agreement with the values obtained by other investigators (See also Table 25, Appendix X). It is seen, for example, that the steady-state velocities obtained in the 1.5-inch diameter tube (3.8 cm) used in this investigation lie between the values uncorrected for wall effects obtained by Berets, Green and Kistiakowsky (17) in their 1.9 cm. and 10 cm. diameter detonation tubes at 1 atmosphere initial pressure. This is to be expected since losses due to wall effects, even though they are small, do cause a decrease in the experimental detonation velocity. Therefore, the velocities obtained in the 3.8 cm tube should logically fall between the 1.9 cm.



and 10 cm. tube values. A more detailed discussion of the influence of wall effects and other effects will be given in a later part of this section.

Also from Figs. 35, 36, and 37 (0% additive lines), and 42 and 43, it is seen that the experimental detonation velocities for stoichiometric hydrogen-oxygen mixtures follow the same trend with increase in initial pressure as the theoretical curve. That is, the detonation velocity increases at a decreasing rate with increase in initial pressure. Also it appears that the general agreement between theoretical and experimental velocities is quite good, at least at initial pressures up to 100 atmospheres. It is seen, however, that at low pressures the experimental velocities lie very slightly below the predicted curves; i. e., approximately 1/4% at 1/2 atmospheres. At the higher initial pressures, the experimental points rise above the theoretical curves. The deviation became greater as the initial pressure increases; i. e., approximately 2-1/2% higher at 50 atmospheres. (See Table 13, Appendix IX). The discrepancies at the low pressures are probably due to oversimplifications in the elementary theoretical model, such as the assumption of a planar discontinuity, chemical and thermal equilibrium, and no heat or momentum losses. The discrepancies at high initial pressures are probably due principally to the use of idealized properties and idealized thermal and calorific equations of state for the theoretical

computations. The imperfections in the theoretical model also apply at these conditions although these effects are undoubtedly masked by the greater effect of non-ideality in the product gases. Further, chemical equilibrium is probably more closely approached at these higher pressures because of the shorter mean free path for chemically-productive collisions. It will be seen ( Figs. 35, 36, and 37 and Table 14 through 24, Appendix IX) that the experimental detonation velocities for the stoichiometric hydrogen-oxygen-additives mixtures considered in this investigation follow the same pattern with initial pressures as the pure stoichiometric hydrogen-oxygen mixture. The probable reasons for the observed deviations of the experimental from the theoretical Chapman-Jouguet velocities for the pure stoichiometric hydrogen-oxygen mixtures, as well as for the additive mixtures, will be discussed in more detail in a later portion of this section.

The experimental detonation velocity curves for pure stoichiometric hydrogen-oxygen mixtures, as well as for the other mixtures considered in this investigation, need not necessarily behave in the same manner as the predicted curves. As the pressure increases without bound, the experimental detonation velocities might increase indefinitely with pressure. Conversely, they might even reach a maximum and decrease thereafter depending upon the effect of pressure on the physical properties of the reactants and products. It is

contended, therefore, that the behavior of the experimental curves cannot be predicted much beyond the experimental range without an accurate knowledge of the physical properties under actual test conditions.

Based on the data obtained in this investigation, it is believed that the simplified thermohydrodynamic theory quite adequately describes the real situation and can be used with confidence to predict the actual detonation velocity in stoichiometric hydrogen-oxygen mixtures at 3 000°K initial temperature and at initial pressures from about 1/2 atmosphere to 100 atmospheres. Below approximately 1/2 atmosphere and above 100 atmospheres initial pressure it is felt that the theory is oversimplified and inadequate. This can be seen by the increasing divergence of the experimental from the theoretical curve (Fig. 42). The reliability of the data calculated on this basis is open to question outside of this range. It will be seen that these limitations hold approximately true for all the additive mixtures considered in this investigation.

For the stoichiometric hydrogen-oxygen mixtures, the deviation at 1/2 atmosphere initial pressure is about -1/4%. At 100 atmospheres, it is about + 4%. It will be seen that the deviations at 100 atmospheres are about the same magnitude for all the mixtures considered in this investigation. However, at the lower initial pressure

of 1/2 atmosphere, the deviation varies from about -1% to -5% for the helium-additive system, -1% to -3% for the argon-additive system, and -1 1/2 to -5% for the carbon dioxide-additive system. The reasons for these deviations and trend in deviations will be discussed in a later portion of this section. (See Section V-E and F).

The theoretical calculations and plots (Fig. 38 through 41-0% additive, Fig. 42 and Table 1, Appendix VIII) show that in the pure stoichiometric hydrogen-oxygen mixture, the theoretical detonation static pressure ratio ( $p''/p'$ ), detonation impact pressure ratio ( $P_z/p'$ ), normal shock wave static pressure ratio ( $P_{NS}/p'$ ), and normal shock impact pressure ratio ( $P_{INS}/p'$ ) follow the expected trend. All increase as the initial gas-mixture pressure increases. It is seen also that the pressures behind the normal shock wave are approximately twice the pressures in the detonation wave and slightly higher than the impact pressures. (Impact pressure ratios were not drawn in to avoid confusion.) The normal shock wave impact pressures are approximately nine times the detonation static pressures. It can be shown from the fundamental thermohydrodynamic equations that for a high velocity detonation wave, the pressure behind the detonation wave should be approximately half of that which could exist behind a normal shock of the same velocity. Thus the results obtained conform to theoretical expectations.

Analysis of values of the theoretical detonation static pressure, detonation impact pressure, normal shock wave pressure and normal shock wave impact pressure shows that these pressures increase linearly with increase in initial pressure. It is interesting to note that based on the NDZ model of a detonation wave utilized in this investigation, short-duration detonation leading edge shock wave impact pressures of about 3,000,000 psi theoretically could be attained in detonable stoichiometric hydrogen-oxygen mixtures initially at 1000 atmospheres pressure (See Table I, Appendix VIII). This terrific pressure, even though of short duration, in conjunction with the fairly respectable detonation temperature of about  $2000^{\circ}$  to  $5000^{\circ}$  K., should be seriously considered in the design of equipment required to sustain gaseous mixtures capable of detonating.

From Fig. 42 and Table 25, Appendix X, it can be seen that only a very few measurements of static detonation pressure in gaseous mixtures have been reported. Also all of these measurements were made at initial pressures of 2 atmospheres and below, the majority being made in pure hydrogen-oxygen mixtures at atmospheric conditions. It is seen further that for the most part there is very little agreement between the reported measured values of static detonation pressure for the stoichiometric hydrogen-oxygen system. This is not too surprising in view of the inaccuracies inherent in some of the

pressure measuring techniques and instrumentation, as well as in some of the means used for interpretation of the pressure data obtained. (Refer to Section II-H2 for additional details.) Probably the most reliable detonation static pressure data reported previously is that of Edwards, Williams and Breeze (103) who used an improved version of the Hopkinson pressure bar method to determine the detonation static pressure in hydrogen-oxygen mixtures at initial pressures of 1 atmosphere. The detonation pressure data on the stoichiometric hydrogen-oxygen mixture in this investigation agree quite well with that of Edwards, et. al. (103).

Agreement between the static detonation results obtained in this investigation and those of Gordon (132, 134) is also seen to be good. It is felt though that the pressure measuring technique used by Gordon (i. e., tourmaline piezoelectric crystal mounted in oil, in conjunction with an oscilloscope.) and his method of calibration and interpretation of pressure data are not very reliable. Also, it is believed by this investigator that in some instances the detonation waves obtained by Gordon were overdriven and had not yet reached steady-state conditions at the time measurements were taken. Thus, even though the pressure data reported by Gordon (132, 134) agree quite well with the theoretical calculations and with the results obtained in this investigation, it is felt that the close agreement of theoretical and experimental results obtained by Gordon was due primarily to a for-

tuitous cancelling of errors inherent in the method used.

From Fig. 42 it is seen that the average experimental detonation static pressure ratios for the stoichiometric hydrogen-oxygen mixtures (See Table 13, Appendix IX) are of the same magnitude and follow the same trend with increase in initial pressure as the theoretical curve; i. e., the detonation static pressure increases with increase in initial pressure. It is seen also that at low initial pressures (i. e., 1 atmosphere) the average detonation static pressure ratio values appear to lie somewhat below the theoretical curve, the deficit decreasing as the initial pressure increases. As the initial pressure continues to increase, it appears that the experimental points rise above the theoretical curve, the deviation increasing as the initial pressure increases. From these observations, it appears that the deviations in the average static detonation pressures follow the same trend with initial pressure as the deviations in the experimental detonation velocity measurements. (See previous paragraphs of this section, Fig. 42 and Table 13, Appendix IX for details). This is the logical and expected trend.

It should be pointed out again that the experimental data presented in Fig. 42 and the curve derived from the experimental points are qualitative only due to the uncertainty in the absolute values of the pressure measurements. Thus, no quantitative determination can

be made of the difference between the theoretical and measured detonation static pressures, since these deviations, in many instances, fall within the range of experimental error associated with the pressure measuring system. (See Table 13, Appendix IX). However, the measurements are seen to be of the correct order of magnitude. Thus they can be used to make qualitative conclusions pertaining to the magnitudes and trends of the detonation static pressure for the various mixtures investigated. (See Section V-A-1 for detailed discussion of experimental pressure measurements.) A general discussion pertaining to the magnitudes and trend of deviations between experimental and theoretical Chapman-Jouguet detonation static pressures are to be expected, (assuming very precise and accurate pressure measurements). The possible reasons for these deviations, and a comparison of these deviations will be discussed in more detail in Section V-B, E, and F for the pure stoichiometric hydrogen-oxygen mixture as well as for the helium-additive, the argon-additive and the carbon dioxide-additive mixtures considered in this investigation.

## 2. Stoichiometric Hydrogen-Oxygen Helium Mixtures

The addition of chemically inactive helium ( or argon) to the stoichiometric hydrogen-oxygen mixture has the effect of reducing the concentrations of all the chemically reactive species in the detona-



tion products. (See Fig. 31 and Tables 2 through 5, Appendix VIII.) The decrease in concentration is proportional to the amount of helium added to the basic mixture ( $2\text{H}_2 + \text{O}_2$ ). It is seen that the water molecule is still the major reaction product supplying the energy supporting the detonation wave. (The additive in some mixtures is a greater mole fraction, but it is considered as a non-participating non-energy producing inert here.) An increase in initial pressure affects the concentration of the chemically-reactive equilibrium product species for all the helium-additive mixtures in the same manner as that noted for the pure stoichiometric hydrogen-oxygen mixtures. That is, the concentration of  $\text{H}_2\text{O}$  increases and the concentrations of the other chemically-reactive components decrease as the initial pressure increases.

It is interesting to note that the same family of curves can be used to represent the theoretical composition of the detonation products of stoichiometric hydrogen-oxygen mixtures admixed with either helium or argon (or any other chemically-inactive inert). This is to be expected since the two inert gases are theoretically identical in every chemical aspect. Thus not only the composition for like percentage additive mixtures theoretically should be the same, but also all other thermodynamic and state properties should be alike.

The addition of chemically inactive helium ( or argon) to the stoichiometric hydrogen-oxygen mixture ( Fig. 33 and Tables 2 through 9, Appendix VIII) decreases the theoretical detonation temperature and density ratio and shock wave density ratio and increases the shock wave temperature. The change in each of these properties is proportional to the percent of helium ( or argon) added to the basic mixture. The temperature and density ratio curves for all the helium- ( or argon) - additive mixtures follow the same trend with initial gas-mixture pressure as the basic stoichiometric hydrogen-oxygen mixture. The changes in the theoretical state properties of the basic stoichiometric hydrogen-oxygen mixture, upon addition of quantities of the inerts of helium ( or argon), are due to the decrease in "available energy" per unit mass of initial mixture. This decrease in "available energy" is due to the "dilution effect" of the inert additives which contribute nothing in the way of energy to help support the detonation wave propagation.

From Fig. 35 and Tables 2 through 5, Appendix VIII, it is seen that the addition of helium to the pure stoichiometric hydrogen-oxygen mixture increases the theoretical Chapman-Jouguet detonation velocity. The increase is proportional to the amount of helium added to the basic mixture. From the ideal thermohydrodynamic relationships it can be shown that the detonation velocity is equal to the density ratio times the speed of sound in the detonation products; i. e.,

$$D = \rho''/\rho' \sqrt{\frac{\gamma_{n(g)} R T''}{m''}} = \frac{\rho''}{\rho'} \sqrt{\frac{\gamma_{n(g)} p''}{\rho''}}$$
 (For purposes of the following analysis, it is simpler and sufficiently accurate to assume that the velocity of the burned gases with respect to the detonation wave is equal to the "frozen" speed of sound at the Chapman-Jouguet condition). Thus, the theoretical detonation velocity is proportional to the density ratio and the square root of the specific heat ratio and temperature of the detonation products and inversely proportional to the square root of the product molecular weight.

Very little difference would be expected between the density ratios ( $\rho''/\rho'$ ) for the stoichiometric hydrogen-oxygen mixture, pure and admixed with helium at the same initial pressure. Also very little difference would be expected between the specific heat ratios ( $\gamma_{n(g)}$ ) in these mixtures. The temperature ( $T''$ ) would be expected to be somewhat lower in the helium-additive mixtures than in the stoichiometric hydrogen-oxygen mixtures, as was seen in the previous paragraphs. The greatest influence on the detonation velocity due to the helium-additive would be due to the effect of the decrease in molecular weight of the detonation products.

In all essence, then, the theoretical detonation velocity in the helium-additive mixtures, to good approximation, is directly proportional to the square root of the product temperature and inversely proportional to the square root of the product molecular weight, or

to the square root of the ratio of the detonation pressure to the product density (i. e.,  $D \propto \sqrt{\frac{I''}{m''}} \propto \sqrt{\frac{P''}{\rho'}}$ ). As indicated previously, the greatest influence on the detonation velocity in these mixtures is due to the product molecular weight. It would be expected, therefore, that the theoretical Chapman-Jouguet detonation velocity in the helium-additive mixtures would increase with increase in percentage of helium, since the molecular weight of the detonation products decreases with increase in helium concentration.

It is seen further that the theoretical detonation velocities increase at a decreasing rate, approaching a velocity asymptote as the initial pressure increases. This is quite similar to that observed for the stoichiometric hydrogen-oxygen mixtures. This, of course, was expected. An increase in pressure would be expected to increase the energy available to support the detonation wave propagation, thus increasing the theoretical detonation velocity as well as the temperature, pressure and density.

The theoretical calculations of Chapman-Jouguet detonation velocities obtained in this investigation are in good agreement with those of other investigators over the limited range of initial conditions where other data was available. (Compare data in Table 25, Appendix X with that in Tables 2 through 5, Appendix VIII.) As in the pure stoichiometric hydrogen-oxygen mixtures the experimental

detonation velocity data obtained follow the same trend with increase in initial pressure as the theoretical curves. Also they appear to be in quite good agreement with the values obtained by other investigators. (See Table 25, Appendix X and Fig. 35). As in the pure stoichiometric hydrogen-oxygen mixtures, it was found, as expected, that the steady-state velocities measured in the 3.8 cm. diameter tube used in this investigation in most instances fell between the values obtained by Berets, et. al. (17) in their 1.9 cm. and 10 cm. diameter detonation tubes.

The agreement between theoretical and experimental detonation velocities, in general, appears to be good over the initial pressure range of  $1/2$  atmosphere to 100 atmospheres. As in the stoichiometric hydrogen-oxygen mixtures, however, at the lowest initial pressure of  $1/2$  atmospheres, the experimental velocities lie slightly below the theoretical curves; i. e., approximately -1% to -5%. The deviation is greatest for the largest percentage helium (50% He) added to the basic system. From the results of this investigation, it appears that the velocity deviations in the helium-additive mixtures are greater than the deviations for the pure stoichiometric hydrogen-oxygen. As will be seen the deviations are also greater than those for comparable argon-additive mixtures in the lower initial pressure range (See Tables 13 through 21, Appendix IX). Also, at the higher initial pressures, the experimental points

rise above the predicted curves, the deviations becoming greater as the initial pressure increases. The deviation is about + 4% at 100 atmospheres initial pressure for any of the helium-additive mixtures considered. This is about the same as for the pure stoichiometric hydrogen-oxygen mixture. (See Tables 13 through 17, Appendix IX and Fig. 35). Discussion of the probable reasons for the deviations and the trend in deviations will be reserved for a later portion of this section. (See Sections V-E and F.)

From Tables 2 through 5, Appendix VIII and Fig. 38 and 39, it is found in conformance with theoretical expectations that the addition of helium (or argon) to the stoichiometric hydrogen-oxygen mixture has the effect of reducing the theoretical detonation static pressure ratio ( $p''/p'$ ), detonation impact pressure ratio ( $P_I^n/p'$ ), normal shock wave static pressure ratio ( $P_{NS}/p$ ) and the normal shock impact rates ( $P_{I_{NS}}/p'$ ). The decrease is proportional to the amount of helium (or argon) added to the basic mixture. However, it is pointed out that only a relatively small change in the magnitude of these parameters is obtained with change in concentration of additive. This indicates that the effect of mixture composition on the detonation and shock wave pressure parameters is small. This holds true in general for all the additive mixtures considered in this investigation.

It is seen further than an increase in initial pressure in these mixtures, as expected, affects the detonation and shock wave pressure parameters in the same manner as that noted for the pure stoichiometric hydrogen-oxygen mixtures. That is, the pressure parameters all increase with increase in initial pressure. Also it is noted as in the basic mixture that the pressures behind the normal shock wave are approximately twice the pressure in the detonation wave and slightly higher than the impact pressures. (The impact pressures were not drawn in to avoid confusion.)

Inspection of Figs. 38 and 39 and Tables 14 through 21, Appendix IX indicates that the average values of the experimental detonation static pressure ratios for the helium-(and argon-) additive mixtures are of the same order of magnitude and follow the same trend with increase in initial pressure as the theoretical curves. This is the same pattern followed by the basic mixture ( $2\text{H}_2 + \text{O}_2$ ). It is seen too that at the lower initial pressures, the average detonation static pressure ratios appear to lie somewhat below the theoretical curves. The deficit decreases as the initial pressure increases and the percent additive decreases. Further, as the initial pressure continues to increase, it appears that the experimental points rise above the theoretical curves, the deviations increasing as the initial pressure continues to increase. (In several

of the higher percentage helium-additive mixtures; i. e., 25 %, 37-1/2% and 50% by volume helium, the experimental pressure curves have not yet crossed the theoretical curve, but the trend is apparent. If tests had been carried out at increased initial pressures, it is believed that they would follow this logical pattern.)

From Figs 38 and 39, it appears also that the deviations between measured and theoretical static detonation pressures follow the same trend with initial pressure and percent additive as the experimental detonation velocity measurements. As pointed out previously, the experimental pressure data obtained and presented in Figs 38 and 39 and the curves derived from them are considered as qualitative only due to the uncertainty in the absolute pressure measurements. Because of this uncertainty no quantitative comparisons can be made between the magnitudes of the pressure deviations for any of the mixtures considered in this investigation.

However, even on a qualitative basis it appears that the experimental pressure data, including the order of magnitude and the trends in deviations, for the helium-additive mixtures follow a logical and expected pattern. If one can assume that any errors involved in the mean values of the detonation static pressure measured are consistent, then any errors involved in the plots of these data should be consistent. On this basis, it appears that the deviations between



the experimental and theoretical detonation static pressure are greater in the helium-additive mixtures than in the basic stoichiometric hydrogen-oxygen mixture. It is seen too (Fig. 38 and 39 and Tables 13 through 21, Appendix IX) that the deviations are also somewhat greater in the helium-additive mixtures than in the corresponding argon-additive mixtures.

### 3. Stoichiometric Hydrogen-Oxygen-Argon Mixtures

The addition of chemically inactive argon to the stoichiometric hydrogen-oxygen mixture has the same effect as the addition of a like amount of helium on the theoretical Chapman-Jouguet equilibrium detonation product and non-reacting normal shock wave thermodynamic and state properties, including composition, pressure, temperature and density ratio. The variation of these theoretically calculated parameters with increase in initial pressure is also the same with argon or with helium as the additive. (See Figs. 31, 33, 38 and 39 and Tables 2 through 9, Appendix VIII). A discussion of these effects, as well as the reasons for the exact similarity between the argon-additive and the helium-additive mixtures, was given in previous paragraphs when the influence of helium-additives was discussed. Thus it will not be repeated here. (See Section VB-2.)

From Fig. 36 and Tables 6 through 9, Appendix VIII, it is seen

that the addition of argon to the pure stoichiometric hydrogen-oxygen mixture decreases the theoretical detonation velocity. The decrease is proportional to the amount of argon added to the basic mixture. As was discussed previously, argon and helium are theoretically identical in every chemical aspect. Thus the theoretical composition and all other thermodynamic and state properties should be alike for like percentage-additive mixtures. It has been shown in the previous portion of this section that the theoretical detonation velocity in the helium-additive mixtures, to close approximation, is proportional to the square root of the ratio of the product temperature over the product molecular weight, or to the square root of the ratio of the detonation pressure to the product density. This relationship holds also for the argon-additive mixtures. Further, since the theoretical detonation temperatures in the two additive-mixture systems containing comparable additive concentrations are the same, the detonation velocity in these two inert gas-additive systems should be inversely proportional to the square root of the product density or the molecular weight. Comparison of the calculated detonation velocities for the helium-and argon-additive mixtures verifies this. (See Tables 2 through 9, Appendix VIII). Thus, it is to be expected that the theoretical detonation velocities in the argon-additive mixtures would be lower than in the corresponding helium-additive mixtures due to the influence of its greater molecular weight.

Theoretical calculations of Chapman-Jouguet detonation velocities are in good agreement with those of other investigators over the very limited range of initial conditions where other data was available. (Compare data from Tables 6 through 9, Appendix VIII with that in Table 25, Appendix X). It can be observed also from Fig. 36 that the experimental velocity data obtained for the argon-additive mixtures are in quite good agreement with the values obtained by other investigators (See also Table 25, Appendix X). As in the pure stoichiometric hydrogen-oxygen and the helium-additive mixtures, it is found, as expected, that the steady-state velocities obtained in the tube used in this investigation (3.8 cm. diameter) in most instances lie between the values obtained by Beret, et. al. (17) in their 1.9 cm. and 10 cm. diameter detonation tubes at 1 atmosphere initial pressure.

Also from Fig. 36 it can be seen that the experimental detonation velocities for the argon-additive mixtures follow the same trend with increase in initial pressure as the theoretical curves. Further the experimental detonation velocities follow the same pattern with increase in initial pressure as the pure stoichiometric hydrogen-oxygen and the helium-additive mixtures. That is, the theoretical detonation velocities increase at a decreasing rate with increase in initial pressure.

In general, the agreement between theoretical and experimental detonation velocities appears to be quite good over the initial pressure range of  $1/2$  atmospheres to 100 atmospheres. As in the pure stoichiometric hydrogen-oxygen and in the helium-additive mixtures, however, at the lowest initial pressures the experimental velocities lie slightly below the predicted curves; i. e., approximately -1% to -3%. The deviation is greatest for the highest percentage argon (50% A by volume) added to the basic mixture. Also, at the higher initial pressures, as in the pure stoichiometric hydrogen-oxygen and helium-additive mixtures, the experimental points rise above the theoretical curves. The deviations become greater as the initial pressure increases. The deviation is about + 4% at 100 atmospheres initial pressure for any of the argon-additive mixtures considered. Discussion of the probable reasons for the observed deviations and the trend in these deviations will be given in a subsequent portion of this section. (See Section V-E and F.)

The addition of argon to the basic stoichiometric hydrogen-oxygen mixture affects the value of the detonation static pressure almost exactly in the same manner as the addition of equivalent amounts of helium. Thus, the experimental measurements of detonation static pressure and the curves derived from these measurements for the argon-additive mixtures, are close to the data obtained for the helium-additive mixtures. (See Figs. 38 and 39 and Tables 14

through 21, Appendix IX). As discussed previously, this is entirely logical and to be expected. The same comments made previously when discussing and comparing the theoretical and experimental pressure measurements in the helium-additive mixtures also hold for the argon-additive mixtures. Therefore, they will not be repeated here.

From Fig. 38 and 39, it appears that there is a small difference in the magnitude of the deviations between the experimental and theoretical detonation static pressures. However, due to the degree of uncertainty in the absolute values of the pressure measurements, it is not possible to make a quantitative comparison of the magnitude of these deviations for these mixtures. Even so, on the basis of the mean values of the detonation static pressure obtained in this investigation, assuming all errors involved are consistent, in general it appears that the deviations are greater in the helium-additive mixtures than in either the basic stoichiometric hydrogen-oxygen mixture or in the comparable argon-additive mixtures. This would be the expected pattern, agreeing with the differences in the deviations in detonation velocity for these mixtures. The magnitude and trend of the deviations to be expected and possible reasons for these deviations will be discussed in more detail in Sections V-E and -F.

#### 4. Stoichiometric Hydrogen-Oxygen-Carbon Dioxide Mixtures

From Fig. 32 and Tables 10 through 12 - Appendix VIII, it is seen that  $\text{H}_2\text{O}$  is also the predominant chemically reactive energy-producing specie in all the stoichiometric hydrogen-oxygen-carbon dioxide mixtures considered, as it was in the helium-and argon-additive mixtures. It is seen further that the concentration of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  increase and the concentration of all other major constituents (i. e.,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{H}$ ,  $\text{OH}$ ,  $\text{O}_2$ , and  $\text{O}$ ) decrease as the initial pressure increases. This is similar to the trend noted for the stoichiometric hydrogen-oxygen-helium or argon mixtures. It can be seen also that all minor constituents considered in the reaction products, with the exception of possibly  $\text{CHO}$  are negligible (mole fractions less than  $10^{-6}$ ) for the mixtures being considered. (i. e.,  $\text{C(g)}$ ,  $\text{C(s)}$ ,  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{CH}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$ ,  $\text{CH}_4$ ,  $\text{C}_3\text{O}_2$ ,  $\text{COH}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{O}_3$ ). The effect of  $\text{CHO}$  becomes increasingly important as the initial pressure increases. The mole fraction of  $\text{O}_3$ , although it is seen to increase with initial pressure, remains below  $10^{-5}$ . It is negligible insofar as its influence on the energy contributing to the support of the detonation wave propagation. It should be noticed in particular that solid carbon did not appear in the detonation products of any of the carbon dioxide-diluent mixtures considered. The effect of increasing the percentage of carbon dioxide-additive is to reduce the concentration of the  $\text{H}_2\text{O}$  and all other major constituents, with the exception of  $\text{CO}$  and  $\text{CO}_2$  which are increased. The changes

in concentrations are proportional to the percentage of carbon dioxide added to the basic mixture.

From Fig. 34 and Tables 10 through 12 - Appendix VIII, it is seen that the addition of chemically-reactive carbon dioxide to the basic stoichiometric hydrogen-oxygen mixture has the effect of reducing the theoretical detonation and normal shock wave temperatures and increasing the detonation and normal shock density ratios. The change in these parameters is proportional to the amount of carbon dioxide added to the basic mixture. The detonation temperatures and shock wave temperatures increase and the detonation and shock wave density ratios decrease with increase in initial gas-mixture pressure. This is quite similar to the trend noted for the helium-and argon-additive systems. However, carbon dioxide has a much greater influence than either of the other additives. Again, the detonation temperatures are seen to be approximately twice the shock wave temperatures, and the normal shock densities are about twice those of the detonation waves. The detonation and shock wave temperatures for the carbon dioxide-additive mixtures are seen to be lower than those for corresponding percentages of argon-or helium-additive mixtures. This is understandable since carbon dioxide has a greater heat capacity, and therefore a greater "dilution effect," than either helium or argon. This effect reduces further the available energy supporting the wave propagation. In addition to the dilu-

tion effect, some of the carbon dioxide is dissociated at the equilibrium conditions of the detonation wave. This reaction is endothermic and thus further reduces the "available energy" supply. Since the temperature is directly proportional to the "available energy," it is to be expected that the detonation temperatures in carbon dioxide-diluent mixtures would be lower than those in helium-or argon-diluent mixtures. This same reasoning applies to the detonation and shock wave pressures in these mixtures, as will be seen in later paragraphs of this section.

As can be seen from Fig. 37 and Tables 10 through 12, Appendix VIII, the addition of carbon dioxide to the pure stoichiometric hydrogen-oxygen mixture decreases the theoretical detonation velocity, the decrease being proportional to the amount of carbon dioxide added to the basic mixture. Further, the decrease in theoretical detonation velocity can be shown to be more than that which would be expected for a pure inert of the same molecular weight with chemical inert characteristics identical to helium or argon. It will be shown that this is a logical and correct trend. As was indicated previously, the detonation velocity is proportional to the density ratio ( $\rho''/\rho'$ ), the square root of the specific heat ratio ( $\gamma''(g)$ ) and the product temperature ( $T''$ ), and inversely proportional to the square root of the product molecular weight ( $m''$ ).



Very little difference would be expected between the density ratio values ( $\rho''/\rho'$ ) for the carbon dioxide-additive mixtures and those for the pure stoichiometric hydrogen-oxygen, helium-additive or argon-additive mixtures. The specific heat ratios ( $\gamma''(g)$ ) for the carbon dioxide-additive mixtures would be expected to be somewhat lower than the stoichiometric hydrogen-oxygen or the comparable helium-additive or argon-additive mixture. Also the theoretical detonation temperature ( $T''$ ) and pressure ( $p''$ ) would be expected to be lower in the carbon dioxide-additive mixtures than in the helium-additive or argon-additive mixtures. The reasons for these were discussed in a previous paragraph of this section and will not be repeated here.

On the basis of the above analysis, the theoretical detonation velocities in the carbon dioxide-additive mixtures would be expected to be lower than those in like percentages of argon-additive mixtures because of the effects of increased molecular weight. Further, due to the difference in chemical and thermodynamic properties of carbon dioxide as compared to the inert additives, as well as to its chemical reactivity and participation in the product chemical equilibrium, as has been seen, lower detonation temperatures and specific heat ratios for the chemically-reactive carbon dioxide-additive mixtures are to be expected. These additional influences contribute to a still further

lowering of the theoretical detonation velocities in these mixtures. Thus due to the additional influences discussed above, it would be expected that the detonation velocities in the chemically reactive carbon dioxide-additive mixtures would be somewhat lower than those predicted by the square root-density or molecular weight rule found applicable to chemically inert additives such as helium or argon.

From Fig. 37, it can be seen that the experimental velocity data obtained for the carbon-dioxide additive mixtures are in good agreement with the values obtained by other investigators over the very limited range of initial conditions where data was available. (See also Table 25, Appendix X.) In addition, it is observed that the experimental detonation velocities follow the same trend with initial pressure increase and that they also follow the same pattern as the pure stoichiometric hydrogen-oxygen, the helium-additive, and the argon-additive mixtures. That is, the theoretical detonation velocities increase at a decreasing rate with increase in initial pressure, gradually approaching a velocity asymptote.

The agreement between theoretical and experimental detonation velocities appears to be quite good over the initial pressure range of  $1/2$  atmospheres to 100 atmospheres. Again, as in the pure stoichiometric hydrogen-oxygen, helium-additive and argon-additive mixtures,

the experimental detonation velocities at the lowest initial pressure considered (1/2 atmosphere) lie below the theoretical curves; i. e., approximately -1-1/2% to -5%. The deficit is greatest for the largest percentage carbon dioxide (25% CO<sub>2</sub> by volume) added to the basic system. From the results obtained in this investigation, it appears that the velocity deviations in the carbon dioxide-additive mixtures at the lower initial pressures are greater than the deficits in comparable helium-additive or argon-additive mixtures.

At the higher initial pressures, the experimental points rise above the theoretical curves. The deviations become greater as the initial pressure increases. The deviation is about + 4% at 100 atmospheres initial pressure. This is about the same as for all the other mixtures considered in this investigation at these initial pressures (See Tables 22 through 24, Appendix IX). Discussion of the probable reasons for the deviations and the trends in the deviations will be given in subsequent portions of this section. (See Sections V-E and -F).

As can be seen from Figs. 40 and 41 and Tables 10 through 12, Appendix VIII, and as expected from the analysis presented in previous paragraphs of this section, the addition of carbon dioxide to the pure stoichiometric hydrogen-oxygen mixture decreases the theoretical detonation static pressure ratio ( $\bar{p}^u/\bar{p}^i$ ), detonation impact

pressure ratio ( $P_2^s/P^i$ ), the normal shock impact pressure ratio ( $P_{1,2}/P^i$ ). The decrease is proportional to the amount of carbon dioxide added to the basic mixture. As with the pure stoichiometric hydrogen-oxygen and the helium-additive and argon-additive mixtures, the effect of increasing the concentration of carbon dioxide in the basic mixture (i. e., the mixture composition) on the detonation and shock wave pressure parameters is small.

It is found also that the decrease in the theoretical detonation and shock wave pressure parameters due to the addition of carbon dioxide is greater than the decrease due to the addition of the same amount of helium or argon to the basic mixture. The reasons for this greater influence of carbon dioxide on the theoretical detonation parameters was discussed in previous paragraphs and will not be repeated here. Suffice it to say that the greater decrease of the theoretical pressure parameters due to the addition of carbon dioxide is logical and is to be expected.

Further, it is seen from Figs. 40 and 41 that the pressure parameters all increase with increase in initial pressure. Also it is noted that the pressures behind the normal shock wave are about twice the pressure in the detonation wave and slightly higher than the impact pressures. This behavior is analogous to that observed for the pure (basic) stoichiometric hydrogen-oxygen mixtures and

the basic mixture admixed with helium or argon. This behavior is quite logical and is to be expected. It is seen too that at the lower initial pressures, the mean detonation static pressure ratios appear to lie somewhat below the predicted curves. The deficit decreases as the initial pressure increases and the percent additive decreases. In this investigation, the initial pressures apparently were not high enough to obtain a complete picture of the detonation static pressure curves for most of the carbon dioxide mixtures. (i. e., 10% and 25% carbon dioxide). The trend in the experimental curves is apparent, however. It is believed that if tests had been carried out at increased initial pressures, the experimental pressure curves obtained would all cross the theoretical curves, similar to the pattern exhibited by the "basic" mixture and the helium-and argon-additive mixtures. Following the cross-over point, the experimental points should rise above the theoretical curves. The deviations should then increase as the initial pressure continues to increase.

As with the other mixtures investigated, from Figs. 40 and 41, it appears that the deviations between the measured and theoretical detonation static pressures follow the same trend with initial pressure as the experimental detonation velocities.

From a purely qualitative viewpoint, based on the curves derived from the mean values of the detonation static pressures obtained

in this investigation, it appears that the deviations between theoretical and experimental values are greater in the carbon dioxide-additive mixtures than in the basic mixture or in the basic mixture containing like amounts of helium or argon. This would be the expected pattern, agreeing with the differences in the deviations in detonation velocity for these mixtures.

### C. Discussion of Speed of Sound in a Reacting Gaseous Mixture

The definition of the sound speed is fundamental to the concept of the stable Chapman-Jouguet detonation. The ideal detonation theory dictates that at the Chapman-Jouguet condition, the detonation velocity, when equilibrium is reached, is equal to the local flow velocity plus the sound speed; i. e. :  $D = U + a$ ,  $M = 1$ . Of fundamental interest is which of the two limiting speeds of sound is the most proper to use for the theoretical calculation of detonation parameters: the "frozen" sound speed (fixed chemical composition, very high frequency sound or very slow chemical reaction and thermal relaxation rates), or the "equilibrium" speed of sound (chemical equilibrium composition, zero sound frequency or infinite chemical reaction and thermal relaxation rates). There has been a considerable amount of disagreement between various investigators on this issue, but to date this question has not been satisfactorily resolved. (See Section II D-4 for a summary of the pertinent viewpoints of other investigators pertaining to this question.)

In this investigation, the Mach numbers of the detonation wave with respect to the product gases,  $M''$ , were calculated for all mixtures and initial pressures considered in this investigation, based on both the "frozen" sound speed ( $a''_{n(g)}$ ) and the "equilibrium" sound speed ( $a''_{r(g)}$ ). These values were compared to the value stipulated by the thermohydrodynamic theory; i. e.,  $M'' \equiv 1$ . (In all cases thermal equilibration of the internal and external degrees of freedom was assumed to have been achieved.) The theoretical Mach numbers based on the "frozen" sound speed ( $M''_{n(g)}$ ) and on the "equilibrium" sound speed ( $M''_{r(g)}$ ), the associated speeds of sound, and the corresponding values of the specific heat ratios ( $\gamma_{n(g)}$  and  $\gamma_{r(g)}$ ) are tabulated in Table 1, Appendix VIII for the pure stoichiometric hydrogen-oxygen (basic) mixtures, in Tables 2 through 5 for the helium-additive mixtures, in Tables 6 through 9 for the argon-additive mixtures, and in Tables 10 through 12 for the carbon dioxide-additive mixtures.

Analysis of the data in these tables indicates that in all mixtures and at all initial conditions considered, the Mach numbers of the detonation wave with respect to the product gases which are based on the "frozen" speed of sound ( $M''_{n(g)}$ ) are somewhat lower than the ideal theoretical value; i. e.,  $M'' \equiv 1$ . On the other hand, those based on the "equilibrium" sound speed ( $M''_{r(g)}$ ) are somewhat

higher than the theoretical value. For the "frozen" Mach number, the difference (deficit) is on the order of -6% for the helium-additive and the argon-additive mixtures (See Tables 1 through 9, Appendix VIII) at the lowest initial pressure conditions considered (i. e., 0.5 atmospheres). The deficit decreases with increase in initial pressure to about -1% at the higher initial pressure conditions (i. e., 100 to 1000 atmospheres. For the same helium-additive and argon-additive mixtures, the difference (increase) in the Mach numbers based on the "equilibrium" sound speed is about + 0.1% at the lower initial pressures and decreases to about + 0.3% at the highest initial pressures considered. For the carbon dioxide-additive mixtures (See Tables 10 through 12, Appendix VIII) the "frozen" Mach number difference (deficit) is about -3% at the lower initial pressures and decreases to about -1% at the higher initial pressures. The difference (increase) for the "equilibrium" Mach number for the same carbon dioxide-additive mixtures is on the order of + 4% for the entire pressure range.

From the results of the theoretical calculations, it appears that use of the "equilibrium" product gas sound speed comes closer to meeting the requirements of the ideal Chapman-Jouguet condition for most of the mixtures considered in this investigation. However, it can be seen that neither the "frozen" or the "equilibrium" speeds of sound completely satisfies the ideal Chapman-Jouguet condition.



The actual theoretical speed of sound in a chemical reacting gaseous mixture lies somewhere between the two extremes. Further, the difference between the values of detonation parameters calculated on either basis should be relatively small. Thus, for all practical purposes it is felt that theoretical values of detonation parameters for the idealized Chapman-Jouguet wave, obtained by using the "frozen" speed of sound (which is considerably simpler) would be quite acceptable.

The comments made in the preceding paragraphs pertain specifically to the idealized steady-state Chapman-Jouguet detonation wave where it is assumed that the product gases are in a state of thermodynamic and chemical equilibrium and where there are no energy losses. With detonation wave propagation in real gases, energy may be dissipated through transport phenomena (i. e., viscosity, thermal conductivity, and diffusion). Because of energy dissipation, the propagation of sound waves in the product gaseous media really represents an irreversible process. In addition to the losses due to transport phenomena, the ideal available chemical energy may be reduced due to the non-attainment of chemical equilibrium of one or more of the product gaseous species at the termination of the reaction zone. Also relaxation effects may be such that only partial or no equilibration of either rotational and/or vibrational degrees of freedom is achieved. (See Section V-E for discussion of

these effects). Clearly, these effects seriously complicate the determination of the real value of the detonation product sound speed.

In order to determine the correct product gas sound speed for the real gas situation, and to assess whether it is closer to the "frozen" or "equilibrium" sound speed, it would be necessary to have detailed information pertaining to the chemical kinetics and thermodynamic relaxation rates for each of the chemical reactions involved. To the knowledge of this investigator, such detailed information is not known for the detonations investigated. Also there are no means available at the present time for obtaining even reasonable estimates for these properties under detonation conditions. In addition, information must be available to permit precise determination of energy dissipation due to transport phenomena. Also precise values of the real gas thermodynamic properties of the initial and product gas species and influences due to other effects must be known.

It is quite apparent then from the above discussion that it would be extremely difficult to resolve the question of which detonation product-gas sound speed is correct for the real gas situation. Experimental verification of any product gas sound speed chosen would be a difficult task also. Probably the best that can be hoped for is to

approach the true answer to this dilemma. Significant contributions toward a proper analysis of this problem would be made if very precise measurements of detonation velocity, detonation static pressure (or density) and temperature could be obtained simultaneously. The measurement of any one parameter alone is not sufficient. Especially is this true of the detonation velocity, since it is an extreme quantity and is quite insensitive to the definition of the speed of sound (93, 248, 249). One of the objectives of the present investigation was to attempt to approach the solution of this problem by measurements of detonation velocity and detonation static pressure. Unfortunately, the pressure measurements obtained are not considered to be precise enough to warrant any quantitative conclusions to be made pertaining to the determination of the correct speed of sound in the product gases. Further refinement of the pressure measuring instrumentation (See Section V-A-1) could provide pressure measurements which would be precise enough to add materially to the quantitative analysis of this problem.

#### D. Discussion of Data Pertaining to the Predetonation Region

The investigation of the predetonation region and transition regions are not a part of the objective of this study. However, it is felt that the information obtained as a consequence of this investigation pertaining to these regions is of fundamental importance and

may assist those working in these particular areas in their efforts towards obtaining a better understanding of the general concept of detonation wave propagation. Mention has already been made of the measurements of wave propagation in some of the mixtures and initial pressures considered in this investigation where the fully-developed steady-state detonation wave had not been attained or where detonation was incapable of being supported. (See Section IV-B for details.) Possible reasons for these conditions were also discussed and will be analyzed further here. Also a discussion will be given of the wave propagation data presented graphically in Figs. 43, 45, 46 and 47. The discussion in particular will involve the build-up region up to the shock front formation (i. e., ignition, deflagration and transition from deflagration to detonation) and the stabilization region. This latter region encompasses the region immediately following the formation of the shock front to the region where steady and fully-developed detonation is achieved. Both the build-up and the stabilization regions have been combined and denoted as the "predetonation" "detonation induction" region by most investigators, (i. e., Bollinger, et. al. (21, 22, 23, 25, 26, 27), Oppenheim, et. al. (235, 238, 239), Egerton and Gates (104), and Durmanois and Lafitte (97). Also the distance traversed by the wave before achievement of the fully-developed steady detonation wave has been denoted as the "predetonation" or "detonation induction" length.

Insofar as this investigator could determine there has been very little information published on the rate of change of the detonation build-up and stabilization regions, or on the so-called predetonation or "pre-induction" lengths in these particular mixtures at elevated initial pressures. Unfortunately, the experiments and instrumentation in this investigation were not designed to measure predetonation lengths accurately. Therefore, exact comparisons with such data obtained by other investigators (21, 22, 23, 25, 26, 27, 104) cannot be made. However, the data obtained in this investigation should suffice to show qualitative trends in the predetonation lengths, as well as trends in the detonation build-up and stabilization regions as influenced by additives and initial mixture pressure.

The data presented in Figs. 43, 45, 46 and 47, are in the form of measured time increments ( $\Delta t$ ) versus the position of the wave in the tube. These increments depict the rate of wave propagation between each two-foot ionization probe interval. The average wave velocity, of course, can be obtained easily from the reciprocal of these time increments. Thus, in all essence, the graphs show the trend in wave velocity along the detonation tube. The "build-up" region is characterized by a relatively low average wave velocity which gradually increases as the wave propagates down the detonation tube until a shock front is formed. At this point the maximum wave velocity is achieved. It would be expected then that the

measured time increments in this region would gradually decrease until a minimum is reached at the velocity peak or transition point. In this region the slope of the " $\Delta t$ " lines will be negative.

In the stabilization region the average wave velocity decreases until finally the steady fully-developed detonation wave is achieved; i. e., the average wave velocity remains constant. In this region the measured time increments ( $\Delta t$ ) would be increasing at a decreasing rate, remaining constant when the steady-state fully-developed detonation wave is achieved. The slope of the time intervals increments ( $\Delta t$ ) in this region will be positive, becoming zero (horizontal) when the steady-state detonation is achieved.

It can readily be seen that the "predetonation" or "detonation induction" lengths are directly related to the rates at which both the "build-up" region and the "stabilization" region are completed. Thus the larger the negative slope of the " $\Delta t$ " curve is in the "build-up" region, or the larger the positive slope is of the " $\Delta t$ " curve in the stabilization region, the longer should be the detonation induction length. The longest induction length would be expected in mixtures under conditions where the build-up region is not completed. This would occur in detonable mixtures where the shock is not yet established in the length of tube available. Such

a circumstance might be expected in mixtures at low initial pressures or in mixtures containing a large percentage of diluent.

From Fig. 43, it can be seen that fully-developed stable detonation in stoichiometric hydrogen-oxygen mixtures was achieved at all initial mixture pressures considered in this investigation. Even at 1/2 atmosphere initial pressure, it is apparent that transition from deflagration to detonation had occurred and that the detonation stabilization process was nearing completion at the first probe position. In fact, it did reach completion somewhere between the first and second probe position, i. e., steady fully-developed detonation attained.

From Fig. 46, for the argon-additive mixtures, it is found that the rate of attainment of stable detonation, as evidenced by the slope of " $\Delta t$ " lines, is less than that for the stoichiometric hydrogen-oxygen mixture. Thus it would be expected that the induction distance for the argon-additive mixtures would be larger than that of the stoichiometric hydrogen-oxygen mixtures at the same initial pressure. It can be observed also that the slope of the " $\Delta t$ " lines decrease with increase in initial pressure and increase with increase in additive concentration. This signifies a decrease in detonation induction length with initial pressure increase and an increase in induction length with increase in additive concentration.

Again, by analysis of the slope of the " $\Delta t$ " lines of Fig. 47, for the carbon dioxide-additive mixtures it can be seen, by comparison with the argon-additive and helium-additive mixtures, that the detonation induction lengths are longer in these mixtures than in the corresponding helium-additive or argon-additive mixtures. As in the other mixtures investigated, the induction length decreases with increase in initial pressure and increases with increase in additive concentration.

It appears that the predetonation length is closely associated with both the magnitude of the deviations of detonation velocity and pressure from the ideal Chapman-Jouguet detonation values, as well as with the detonation limits. Thus it appears that predetonation lengths are intimately dependent upon the shock and reaction temperatures, the speed of sound of the product gases, the magnitude and rates of chemical energy release, the effective reaction zone width, the energy losses due to wall effects and other effects (See Sections V-E and F.) For example, it is seen that in those mixtures capable of supporting detonation, where the predetonation length is the longest, (i. e., the carbon dioxide-additive mixtures) the deviations (deficits) are the largest. (See Tables 13 through 24, Appendix IX and Figs. 35 through 42.) It has been seen that in these mixtures the energy losses are relatively large and the temperature and reaction rates are the lowest of all the mixtures considered (See Section V-E and F).



It is seen also that if the predetonation lengths become too long the detonation propagation becomes erratic and nonreproducible. For example, in some of the helium-additive and carbon dioxide-additive mixtures, (i. e., 25% and 37-1/2% helium at 1/2 atmosphere initial pressure; 10% carbon dioxide at 1/2 atmosphere, and 25% carbon dioxide at 1 atmosphere) the wave was still in the build-up stage during its entire propagation through the detonation tube length. (See Figs. 45 and 47). In this mixture ignition was difficult, and the measurements of wave velocity were erratic and not reproducible at each measurement station. It would appear that this was the result of the generally unstable make-up, including the non-planarity and non-repeatability, of the combustion waves in the build-up region. This again is closely associated with effects mentioned in the previous paragraph.

Finally, if the predetonation length exceeds a critical value, detonation cannot be sustained at all. This apparently is a function of the mixture composition, initial pressure and temperature and tube diameter. In these cases it would appear that the rate of energy losses is greater than the rate of energy addition required to form or sustain a stable detonation, and the detonation is quenched. Apparently this occurred in the 50% carbon dioxide-additive mixtures over the entire range of initial mixture pressures considered; (See Fig. 47) and in the 50% helium-additive mixture at 1/2 atmosphere

(See Fig. 45).

To summarize the above discussion, it can be said that addition of helium, argon or carbon dioxide to a stoichiometric hydrogen-oxygen mixture increases the detonation induction distance, the increase being directly proportional to the additive concentration and inversely proportional to the initial mixture pressure. Further, the addition of carbon dioxide causes the greatest increase in the detonation induction distance, while the addition of argon gives the least increase for a given percentage of additive. These observations are in good agreement with those reported by Bollinger, et. al. (23, 26), Egerton and Gates (104), Lafitte, et. al. (97), and others. Finally, it appears that the predetonation lengths are closely associated with the deviations between the experimental and theoretical values of detonation parameters, and particularly the detonation velocity and detonation static pressure.

#### E. Analysis of Deviations Between Experimental and Theoretical Values of Chapman-Jouguet Detonation Velocities and Pressures

It can be observed from Figs. 35 through 42 and Tables 13 through 24, Appendix IX, that for all gaseous mixtures considered in this investigation the experimental curves of detonation velocity and detonation static pressure as a function of initial pressure follow the general

characteristics of the theoretical curves. It can be seen further that in all mixtures investigated, the experimental detonation velocities and pressures in the lower initial pressure range are somewhat lower and in the higher initial pressure range they are somewhat higher than the theoretical Chapman-Jouguet values. Also the deviations progressively increase as both extremes of the initial pressure range are approached.

The differences between the experimental and theoretically calculated Chapman-Jouguet detonation velocity and pressure may be due to one or more of the following effects:

1. Real gas effects, including both thermal and calorific non-ideality;
2. Energy losses due to mass diffusion;
3. Energy losses due to wall effects, including losses due to friction (viscous) and heat conduction;
4. Two-dimensional effects;
5. Energy losses due to radiation;
6. Non-attainment of thermal equilibrium;
7. Non-attainment of chemical equilibrium;
8. Chemical reaction in the shock front or in the induction zone;
9. Non-planarity and multi-dimensional characteristic of the detonation wave, i. e., wave front irregular and changing in orientation as wave propagates down detonation tube.

The influence of each of the above effects on the values of the detonation parameters, in particular the values of the detonation velo-

city and pressure, will be discussed in the following paragraphs.

### 1. Real Gas Effects

It would be difficult indeed to make a quantitative determination of the errors introduced into the calculated Chapman-Jouguet detonation velocities, pressures, temperatures and other parameters by using the perfect-ideal gas thermal and calorific equations of state (i. e.,  $p = \frac{pRT}{m}$ , and thermodynamic properties a function of temperature only.) instead of the real gas equations of state, considering the gaseous products to be thermally and calorifically imperfect at high temperatures and pressures. (i. e.,  $p = \frac{ZRT}{m}$ , and the thermodynamic properties a function of both temperature and pressure.)

In order to make such an error analysis, data would be required giving the effect of pressure on the thermodynamic properties (i. e., enthalpies, specific heats, free energies or fugacity coefficients and the compressibility factors) for the components in the product gases as a function of temperature and pressure. No data were located giving the effect of pressure on these properties or on the compressibility factor and fugacity coefficients at the higher pressures for which computations were made in this investigation. A small amount of high pressure data were found for a few of the product species. However, the data in general did not go to a high enough temperature. Also generalized charts using reduced temperatures and pressures

did not in general go high enough. It was primarily for these reasons that the detonation computations performed as part of this investigation utilized the ideal gas equation of state and idealized thermodynamic properties.

Rather than attempt a quantitative error analysis, which would possibly be of dubious validity, it was decided instead to obtain a qualitative indication of the change in the value of the detonation parameters due to the use of real gas equations of state. To accomplish this objective a simple detonation model was improvised consisting of a shock wave propagating through a single pure gaseous media (oxygen) intimately coupled with and supported by energy supplied from some energy source. (A shock wave coupled to an energy source in all essence can be considered to be a detonation wave.) (All gases, in general, behave approximately the same insofar as their deviation from ideality under high pressure conditions. Therefore, the analysis made should also show the trend of calculated detonation parameters for all the gaseous systems considered in this investigation). It was assumed, as a first order approximation that the composition of the system remained invariant at both the initial and final states; i. e., no dissociation or ionization. It was also assumed that there were no losses due to transport properties and that the system was in complete thermal equilibrium; i. e., complete relaxation prevailed in the internal modes of motion of the product

species. Further, it was assumed that only the intermolecular forces (van der Waals forces) were important and that coulomb forces, etc., were negligible insofar as the real gas thermal equation of state was concerned.

For this analysis the (Rankine-) Hugoniot energy equation obtained by the combination of the conservation of mass, momentum and energy equation across the detonation wave (See Eq. AII-4, Appendix II was recast so as to include an energy addition term,  $q$  (cal/gm),

$$h''(T, p) - h'(T, p) - q = 1/2 \rho'/\rho'' (\rho''/\rho' - 1) (1 + \rho'/\rho'') \quad (\text{V-1})$$

and to indicate the dependency of the enthalpy upon both pressure and temperature for the real gas situation. (The enthalpy, of course, is also dependent upon the composition. However, since the composition in the model being analyzed has been assumed constant, this restriction is not required.) The enthalpy terms contain implicitly some density and pressure terms, thus a thermal equation of state must be used to relate the pressure, temperature and density ( $p, T, \rho$ ) to permit a solution of the Hugoniot relationship. In addition, of course, a calorific equation of state is required to permit determination of the enthalpy as a function of pressure and temperature for the real gas condition. It is obvious that the forms of the thermal equation of state as well as the caloric equation of state will determine the form of the (Rankine-) Hugoniot curve. Therefore, they will de-

termine the value of the slope of the Rayleigh line at the Chapman-Jouguet point, the Chapman-Jouguet detonation pressure, velocity, temperature, density and other detonation properties.

In this analysis the following equations of state were used:

For the ideal perfect gas:

$$\text{Thermal Equation of State: } p = \frac{\rho RT}{m} \quad (V-2)$$

$$\text{Caloric Equations of State } E^0 = f(T) = \int_T^{T''} C_V^0 dT + E^0 \quad (V-3)$$

$$H^0 = f(T) = \int_T^{T''} C_p^0 dT + H^0 \quad (V-4)$$

$$H \equiv E + pV. \quad (V-5)$$

For the real gas:

$$\text{Thermal Equation of State } p = \frac{z \rho RT}{m} \quad (V-6)$$

where  $z = f(T, p) = \text{compressibility factor}$

Caloric Equations of State:

$$\int_H^{H''} dH = \int_T^{T''} C_p^0 dT + \int_p^{p''} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp = (H - H_0)_p + (H - H_0)_T \quad (V-7)$$

(TEMPERATURE EFFECT) (PRESSURE EFFECT)

The pressure effect on enthalpy can alternately be expressed by the following equations through the use of the real gas thermal-equation of state ( $p = \frac{z \rho RT}{m}$ ) and the reduced properties, ( $p/p_c = p_r$ , and  $T/T_c = T_r$ ) (86, 160).

$$\left( \frac{H - H^0}{T_c} \right)_T = RT_r^2 \int_0^{p_r} \left( \frac{\partial z}{\partial T_r} \right)_p d \ln p_r \quad (V-8)$$

Values of  $Z$  and  $\left(\frac{H^0 - H}{T_c}\right)$  are plotted in terms of reduced conditions in Dodge ( 86) and Hougen and Watson ( 160). These charts were used to obtain corrections for enthalpy and values of the compressability factor due to real gas effects.

Substituting into the Hugoniot equation ( Eq. V-1) the real gas thermal equation of state  $(p = \frac{Zp^0}{m})$ , to eliminate the densities gives

$$\frac{m'}{ZRT'} [h''(T,p) - h'(T,p) - q] = 1/2 \left( \frac{p''}{p'} - 1 \right) \left( 1 + \frac{Z'p'm'T''}{Z'p''m''T'} \right) \quad (V-9)$$

for the ideal case, of course,  $Z' = Z = 1$  and  $h = f(T)$ ; and Eq. ( V-9)

becomes

$$\frac{m'}{RT'} [h''(T) - h'(T) - q] = 1/2 \left( \frac{p''}{p'} - 1 \right) \left( 1 + \frac{p'm'T''}{p''m''T'} \right) \quad (V-10)$$

Using these two equations, the Hugoniot curves for the simplified model of detonation assumed were obtained for both the ideal and the real gas cases. The Hugoniot equation was solved by a trial and error procedure, finding the appropriate values of  $p''/p'$  and  $\rho'/\rho''$  at various selected values of  $T''$  which would satisfy the equation. It was found that in the real gas case the enthalpy of the system at the final state ( $h''$ ) was increased above that for the ideal gas due to the influence of pressure. For a fixed amount of energy addition, then the total energy available for support of the curve propagation ( $h'' - h' - q$ ) was greater for the real gas situation than for the ideal gas. Thus, a larger  $p''/p'$  and smaller  $\rho'/\rho''$  was required at a chosen temperature to satisfy the Hugoniot equation for the real gas situation.



The overall effect of this is to shift the real gas dynamic adiabatic or Hugoniot curve above that for the ideal gas situation. This is much in the same manner that the Hugoniot curve is shifted upward and above the pure shock wave dynamic adiabatic (See Fig. 1,  $N=0$ , no energy addition) as the reaction precedes to equilibrium ( $N=1$ ); i. e., equilibrium Hugoniot for a chemically-driven shock wave or detonation wave. As a consequence of the increased energy available due to pressure effects, it was found also that at the Chapman-Jouguet point, the value of the detonation pressure ratio, the slope of the Rayleigh line and therefore the value of the detonation velocity was greater for the real gas situation than for the ideal gas case.

The main conclusion to be derived from the results of the analysis of this simplified non-reacting detonation model is that use of the real gas thermal and caloric equations of state instead of the ideal gas equations of state would have increased the values of the calculated Chapman-Jouguet detonation pressure, temperature, velocity and density, especially at the higher initial and final pressures where the influence of pressure is most prominent. This is the region where the experimental stable detonation velocities obtained were higher than the theoretical data based on ideal gas assumptions. Inclusion of real gas corrections based on the simplified model chosen, therefore, would tend to decrease the deviation between theoretical and experimental velocity data obtained in this investigation.

It is realized, of course, that real gas effects also influence the free energy and the fugacity coefficients, and therefore the equilibrium constants and the product mole fractions. The effect on the equilibrium composition of the detonation products was not considered in the above simplified model. To determine qualitatively the effect of pressure on the equilibrium product composition, and therefore on the value of the detonation parameters, an analysis was made of the water equilibrium reaction. This is the most important of the reaction products in the systems considered in this investigation. It was assumed that the water was at 1000 atmospheres and 4300°K., simulating the conditions in a stoichiometric hydrogen-oxygen detonation at an initial pressure of 50 atmospheres.

From the plots of the ratio of fugacity to pressure or fugacity coefficient ( $\gamma = f/p$ ) against reduced temperature and pressure, presented in Hougen and Watson (160) and Dodge (86), values of the fugacity coefficients for  $H_2$ ,  $O_2$  and  $H_2O$  were obtained at the assumed temperature and pressure. Using these values the equilibrium constant in terms of activity coefficients ( $K_\gamma$ ) was determined. Then the ratio of the equilibrium constants in terms of fugacity ( $K_f$ ) and the equilibrium constant in terms of partial pressures ( $K_p$ ) was obtained from the relationship:  $K_f/K_p = K_\gamma$ . It was found that  $K_\gamma$  for the water reaction at the chosen conditions was slightly greater than unity, (i. e.,  $\gamma_{H_2} \cong \gamma_{O_2} \cong 1$ ;  $\gamma_{H_2O} \cong 1.03$ ). This indicates that the in-

fluence of pressure under the assumed conditions (non-ideal gas effects) would be to increase somewhat the "effective" pressure. Thereby the mole fraction of water formed in the detonation reaction products would be increased. This in turn would cause an increase in the amount of energy available to support the detonation and thus increase the detonation velocity, pressure, temperature, and density above that calculated by means of the ideal gas assumptions. Thus real gas corrections applied to this particular equilibrium reaction would also tend to decrease the deviation between the experimentally determined and the calculated values of the measured parameters.

Since the critical properties of H, O, and OH are not known, no attempt was made to analyze the influence of pressure on the equilibrium reactions for their formation, their enthalpy or compressibility factors. It is entirely possible that the influence of pressure on these constituents could be such as to act in opposition to the other effects analyzed above. Thus a smaller net error could be left than might be anticipated in the computed detonation parameters using ideal gas assumptions.

At the lower range of initial pressures, (i. e., up to  $p' = 5$  atmospheres and  $p'' = 100$  atmospheres) the compressibility factors based on the mole average of the compressibility factors of the

constituents in the initial and in the final mixtures were found to be very close to unity (i. e.,  $Z' = Z'' = 1.0$ ). It was also determined that corrections to enthalpy and the equilibrium constants ( $K_p$ ) due to real gas effects were negligible in comparison to the changes encountered in these quantities at the higher range of initial and final pressure conditions discussed in the paragraphs above. It appears then that all the gas mixtures considered in this investigation can be assumed to behave as ideal gases in the lower initial gas-mixture pressure ranges (i. e., calorically and thermally perfect). Thus, real gas effects should have very little influence on the values of the detonation parameters of these lower initial gas-mixture pressure ranges.

## 2. Analysis of Trend of Deviations in Detonation Parameters at High Initial Pressures of Stoichiometric Hydrogen-Oxygen-Additive Mixtures with Increase in Additive Percentage.

The real gas analysis made in a previous portion of this section was extended in order to explain the trend in the deviations between theoretical and experimental values of the Chapman-Jouguet detonation parameters with the addition of increasing amounts of the different additives (helium, argon, or carbon dioxide) at the higher range of initial pressures considered. For this analysis, as a first order approximation, it was assumed that for all the gaseous mixtures under consideration, both chemical and thermal equilibrium are achieved (or at least are achieved to the same degree) at the Chapman-Jouguet

condition and that dissipation due to transport properties, (i. e., diffusion, heat transfer, etc.) are negligible. It is believed that these approximations are reasonable, especially at the high pressure conditions considered, (i. e., on the order of 50 atmospheres initial pressure and 1000 atmospheres final detonation pressure) since the reaction zone width decreases greatly as the pressure and temperature increase (i. e., the reaction rates and statistical combination rates are increased). Also in the case of additives, the chemical combination rates are increased still further due to their third-body effect. This effect enhances further the approach to theoretical chemical and thermal equilibrium of all chemical reactions and species involved.

Thus, it would appear that the trend in the deviations between theoretical and experimental values of the detonation parameters for the additive systems, at the higher pressure conditions, can be related directly to the differences in the compressibility factors ( $Z'$  and  $Z''$ ) in the real gas equation of state, and to the differences in the enthalpy corrections due to pressure effects ( $H-H^0$ ) for the predominant energy-producing reaction product ( $H_2O$ ) and the additive.

Assuming the gas mixtures to be initially at 50 atmospheres pressure and 300°K., the compressibility factors for the initial

mixture ( $Z_i$ 's) were approximated as the mole average of the compressibility factors of the constituents in the initial mixture. For these calculations use was made of the generalized charts of compressibility factor as a function of reduced temperature ( $\frac{T}{T_c} = T_R$ ) and pressure ( $\frac{P}{P_c} = P_R$ ) presented by Hougen and Watson (140), Dodge (86) and Watson and Smith (306). The compressibility factors for all the mixtures considered in this investigation at this initial condition were found to be very close to unity, (i. e.,  $Z_i = 1.0$  for all mixtures at these initial conditions).

For all the gaseous mixtures considered in this investigation, at initial conditions of 50 atmospheres and 300°K., the final Chapman-Jouguet detonation pressure and temperature were about 1000 atmospheres and 4000°K., respectively. However, using the actual theoretically calculated Chapman-Jouguet values for each mixture instead of these average values, the average compressibility factors of the burned mixtures ( $Z_i$ 's) were approximated using the mole average of the compressibility factors of  $H_2$ ,  $O_2$ ,  $H_2O$ , and the additive (He, A, or  $CO_2$  and CO) for this purpose. (Since the critical properties of O, H, OH and most of the other short-lived species are not known, it was assumed that the compressibility factors of the burnt mixture ( $Z_i$ 's) would at most be that of  $O_2$  or  $H_2O$ ). The average compressibility factors ( $Z_i$ 's) at the final conditions for all the mixtures considered in this investigation

were all found to be about 1.05.

From the above analysis it was concluded that the trend in the deviations between experimental and theoretically calculated Chapman-Jouguet parameters due to the addition of increasing amounts of additives to the "basic" system ( $2\text{H}_2 + \text{O}_2$ ) could be ascertained essentially from the knowledge of the differences in the enthalpy correction due to pressure effects,  $(H-H^0)_T$ , of the energy-producing reaction products (primarily  $\text{H}_2\text{O}$ ) and the diluent.

Using reduced properties and the plots of  $\left(\frac{H-H^0}{T_c}\right)_T$  from Hougen and Watson (160) and Dodge (86), the enthalpy corrections for  $\text{H}_2\text{O}$  and the additive (He, A, or  $\text{CO}_2$ ) admixed with the "basic" gas mixture ( $2\text{H}_2 + \text{O}_2$ ) were determined for each of the additive mixtures at the theoretically calculated Chapman-Jouguet detonation temperature and pressure commensurate to the initial pressure and temperature condition of 50 atmospheres and  $300^\circ\text{K}$ .

It was found that as the percent of any of the additives increases, the difference between the enthalpy correction,  $(H-H^0)_T$ , for  $\text{H}_2\text{O}$  and that for the additive decreases. Thus the overall amount of energy increase due to high pressure effects on the enthalpy of the product gas is decreased due to the addition of any of the additives considered in this investigation. The decrease is proportional to

the increase in amount of additive involved. It was found also that additions of carbon dioxide were more effective in reducing the amount of available energy per gram of mixture than argon, and that argon was somewhat less effective than helium in this respect. The energy available determines the temperature, pressure, velocity and temperature of the detonation wave. Thus, it can be seen on the basis of the above analysis that as the percentage of any of the additives considered is increased, the detonation velocity and pressure should decrease and the experimental values should approach the values calculated by means of ideal gas assumptions at the higher pressure conditions. Also from this analysis the deviations between the experimental and ideal values of detonation velocity and pressure should be greater (percentage wise) for the carbon dioxide-additive system than for the helium- or argon-additive systems. Also the deviations for the helium-additive system should be somewhat greater than those for argon-additive systems for the same percent additive. Inspection of the plots of theoretical and experimental detonation velocities and pressures ( Figs 35 through 42) and the tabulations of theoretical and experimental velocity and pressure results ( Tables 13 through 24, Appendix IX) indicate that this is the case. Thus it appears that the simplified analysis made based primarily on corrections to enthalpy due to real gas effects does indeed explain the trend of the deviations of the experimental from the calculated detonation parameters with increase in percent



additive at high pressures.

It can be stated therefore that from the analysis made in this section that at the higher pressure range the detonation velocity and pressure decrease as the percent additive increases. Also the deviations between experimental and theoretical velocity and pressure data appear to decrease with increase of additive at these higher pressure conditions.

### 3. Deviations Due to Transport Phenomena

#### A. General

In a deflagration, transports of mass ( in the form of active radicals) and energy from the burned to the unburned gas is a significant portion of the energy released by the reaction. On the other hand, in detonation waves there are two possible mechanisms to consider. The initial compression in the shock front increases the temperature and pressure to relatively high values in a distance on the order of several mean free paths. Then the main portion of the reaction occurs. Mass and energy transport, while occurring, may or may not be important. If the shock-produced temperature jump is sufficiently high to initiate a reaction immediately, then transport of mass or energy from the burned gases will contribute a negligible portion to the reaction rate; i. e. , very high reaction rates and correspondingly small reaction zone widths. If, however, the temperature,

and thus the reaction rate, is not high enough (resulting in relatively wide reaction zones accompanied by a boundary layer), the energy transferred from the burned gas may be a significant fraction of the available chemical energy. In this instance, the transport effects are important. It would appear then that in detonation waves which have relatively small heat releases, and thus relatively low wave Mach numbers with corresponding small temperature increase across the shock portion of the wave, the transport effects should be more important than in waves where the heat release is relatively very large, and hence the temperature at the beginning of the reaction is much greater. It follows then that transport effects should be most prominent in detonable gaseous mixtures admixed with large amounts of diluents or additives at relatively low initial gas-mixture pressures. In these mixtures the detonation temperature and reaction rates are relatively lower and the reaction zones and boundary layers are relatively larger than those corresponding to mixtures with little or no additives at high initial pressures.

#### B. Deviations Due to Diffusional Transport Effects

As can be inferred from the above discussion, a portion of the deviations between the theoretical and experimental values of detonation velocity and pressure obtained in this investigation might possibly be attributed to mass diffusion of species in the reaction zone. The only species which could possibly be of concern in connection with

mass diffusion in the detonation waves considered in this investigation are the light constituents which have the highest diffusion coefficients, such as hydrogen. However, even at the lowest initial gas-mixture pressure and highest additive concentration considered in this investigation (which are the conditions where such effects would be most influential), the rates of mass propagation experienced in the detonation wave were undoubtedly much faster than the mass diffusional rates. Therefore, it is highly improbable that much if any significant diffusional transport would take place. Thus, it is the opinion of this investigator that the influence of mass diffusion transport is quite small in any of the mixtures and at any of the test conditions considered in this investigation. Further, it is felt that its influence on the values of the detonation parameters undoubtedly is less than that due to thermal transport. Energy losses due to thermal and momentum transport ("wall losses") will be discussed in the next paragraphs.

### C. Energy Losses Due to Wall Effects

Kistiakowsky and co-workers (17, 47, 181, 182, 184, 186), Edwards, Williams and Greene (103), and Gordon and Mooredian (134), attributed the differences between experimental and theoretical velocities, at about ambient initial pressure and temperature conditions, primarily to energy losses to the detonation tube wall in conjunction with incomplete attainment of chemical and thermal

equilibrium in the Chapman-Jouguet plane. In particular, Kistiakowsky, et. al. (17, 47, 181, 182, 184, 186) maintained that energy losses to the walls were produced by heat conduction and friction (Radiation was shown to be insignificant). Further, it was pointed out that ordinary heat conduction was not fast enough to reduce the temperature of the detonation gases appreciably in the few microseconds that count. Instead it was postulated that the energy losses were caused by the instantaneous cooling of a layer of gas in contact with the cold wall and by friction at the wall, causing a reduction of mass velocity in the proximity of the wall. Both effects, it was reasoned, would give rise to a rarefaction wave that would propagate into the interior of the tube with the acoustic velocity of the hot gases. If this occurs within the chemical reaction zone, the resulting energy losses would cause a lowering of the temperature. This in turn would reduce the rate of chemical reaction, and thus reduce the amount of energy available for wave propagation, thereby causing a lowering of the detonation velocity. At the same time, Kistiakowsky's hypothesis necessarily implies a lowering of the static detonation pressure. This is in agreement with the experimental measurements of static pressure obtained in this investigation.

Kistiakowsky, et. al. (17, 47, 181, 182, 184, 186) in their analysis considered the detonation wave to be steady, planar and one-dimensional. No consideration was given to any influences due

to possible viscous boundary layer growth in the reaction zone, i. e., two-dimensional effects. On the other hand, Fay (118, 119, 120, 122) attributed the observed velocity deficit primarily to two-dimensional effects, engendered by the viscous boundary layer wall friction and heat transfer. Fay considered that the growth of the viscous boundary layer on the tube wall was responsible for a uniform divergence of flow in the reaction zone of the detonation front thus changing the propagation from a one-dimensional to a two-dimensional phenomena (i. e., two-dimensional curved front wave). Fay's approach is quite similar to that used by recent investigators (90, 129, 158, 168, 222, 270, 296) in their analysis of attenuation phenomena in shock waves. This phenomena occurs when the shock heated gas loses energy primarily in the turbulent boundary layer created between the inviscid flow and the shock tube wall with subsequent exchange of frictional and thermal transport losses. It would appear that the energy losses due to wall effects in detonation waves are indeed similar to the attenuation phenomena observed in shock waves. However, detonation wave phenomena has an additional contribution which makes it different from the shock wave: energy addition in the form of chemical energy in the reaction zone.

It is the contention of this investigator that the two-dimensional model postulated by Fay and the mechanism of energy losses due to wall effects are quite rational. These appear to be more reasonable

than those hypothesized by Kistiakowsky at low pressures ( ambient and below) where it has been shown (91, 119, 120, 218, 219) that the detonation wave can no longer be considered to be one-dimensional. However, the hypothesis of Kistiakowsky, et.al., should not be discounted entirely for certainly here there is a unique reasoning for accounting for chemical energy losses due to the premature appearance of a very rapid expansion wave in the reaction zone. ( Energy losses due to non-achievement of chemical equilibrium in the reaction zone will be discussed in a subsequent paragraph).

The boundary layer thickness is quite strongly dependent on pressure, the thickness decreasing rapidly as the initial pressure increases. The boundary layer (two-dimensional) influences also decrease as the tube diameter increases. The reaction zone width also decreases ( temperature and rates of reaction increase) with increase in pressure, leaving less surface area for any thermal and frictional losses to the walls. Thus, it is not too surprising that energy losses due to wall effects and two-dimensional effects decrease and thus their influence on the values of detonation parameters decrease, as the initial pressure and tube diameter increase. This, of course, is in accord with experimental observations of velocity deficit, which will be discussed in the following paragraphs.

Energy losses in the detonation wave reaction zone ( see Figs. 28 and 29) due to wall effects have been found ( 17, 81, 87, 88, 118, 120, 122, 134, 143, 186, 223, 225, 282, 283, 284, 285, 319, 320, 321, 322) to cause a decrease in the experimental detonation velocities; i. e. , "velocity deficit." ( Wall effects should also decrease the experimental detonation static pressure in the same manner as the velocity. The "wall effect" on pressure has not been investigated as yet to the knowledge of this investigator. This would make a good independent research project in itself). That this loss of energy should cause a decrease in the detonation velocity ( and pressure, temperature and density) is logical, for this dissipated energy is not available for the support of the detonation wave propagation. Kistiakowsky and co-workers ( 17, 186), Moyle, Morrison and Churchill ( 225), and others found that the velocity deficit was inversely proportioned to the tube diameter. Moora-dian and Gordon ( 134, 223) and Fay ( 118, 119, 120) found further that the velocity deficiency due to wall effects should be inversely proportioned to the initial pressure. A number of investigators ( 127, 225) who conducted investigations in hydrogen-oxygen mixtures have obtained the following relationship for the "wall effect" correction by extrapolating their curves of experimental velocity versus reciprocal of tube diameter to zero reciprocal tube diameter. This relationship is apparently only slightly dependent on mixture composition ( 178, 179):  $D \propto D + \frac{11.8}{d_{\text{tube}} P}$  ( V-11)

where "d" is the tube diameter in inches,  $p'$  is the pressure in atmospheres,  $D_{\infty}$  is the detonation velocity in meters/sec. corrected to infinite diameter, and  $D$  is the measured velocity. Other investigators (48, 118, 119, 120, 182) have established that the wave thickness is proportional to the inverse square of the initial pressure. If it can be assumed that the tube wall effects increase as the wave (reaction zone) increases, it appears that the correction due to wall effect may not be as large as indicated by the above equation. It would seem to this investigator that the correction should be inversely proportional to the initial pressure raised to some exponent greater than 1 and possibly less than 2. In any event, the corrections due to wall effects for the stoichiometric hydrogen-mixtures considered in this investigation, according to the above equation, were relatively small. They varied from 16 meters/sec. at 1/2 atmosphere pressure to 0.16 meters/sec. at 50 atmospheres initial pressure. These values correspond to less than 0.6% at 1/2 atmosphere and less than .006% at 50 atmospheres, respectively, of the measured velocity. This correction would be proportionately less (except at sub-atmospheric pressures) if the exponent of pressure in the above equation (Eq. V-11) were greater than 1. The same relationship given above should apply with some small change in the correction coefficient for the stoichiometric hydrogen-oxygen-additive mixtures considered in this investigation.

From the above analysis, it is seen that if the corrections due



to "wall effects" were taken into consideration, the theoretical calculated values of detonation velocity and pressure at the lower initial pressures ranges, where the wall effects are most prominent, would be closer to the experimental values. From Eq. V-11, it is seen that the "wall effect" correction decreases rapidly with increase in initial pressure. Thus the correction applied at the higher pressure conditions would have insignificant influence on the values of the detonation parameters.

From the preceding discussion, it can be seen that energy losses due to momentum (friction) and thermal transport to the detonation tube walls are predominately a low pressure phenomena. They are associated with gaseous mixtures at relatively low initial (and final) pressures (and temperatures) where the reaction zones are relatively wider and the reaction rates are relatively lower than those associated with the higher pressure conditions. Also, although they are present at higher initial pressures, they are relatively insignificant in comparison to other effects, such as real gas influences. It will be seen that these same conclusions hold for energy losses due to non-achievement of chemical equilibrium at the termination of the reaction zone; i. e., at the Chapman-Jouguet point.

#### 4. Energy Losses Due to Radiation

Radiation to the detonation tube walls from the hot reacting gases

in the reaction zone could be a source of energy loss which would be instrumental in reducing the experimental detonation velocity and pressure. Unsymmetrical molecules, such as water vapor and carbon dioxide, possess radiative characteristics which possibly should be considered. However, in the opinion of this investigator, the radiation heat transfer of these species in the reaction zone to the relatively clean and bright stainless steel detonation tube walls (low emissivity) is normally only a small portion of the overall loss of energy due to friction and thermal transport losses to the walls. This opinion is shared by other investigators (17). Thus, although losses due to radiation certainly are present in the detonation phenomena, their influence on the values of the detonation parameters is normally negligible.

##### 5. Deviations Due to Non-Attainment of Thermal Equilibrium

It has been assumed in the calculation of the Chapman-Jouguet detonation parameters that the external (translation) and all internal (rotational, vibrational, electronic) degrees of freedom for all species in the initial gaseous mixture and in the detonation products were in complete thermal equilibrium. There may be a possibility, however, that only partial internal energy equilibration is achieved during the induction time period and during the reaction time period associated with the steady detonation wave (See Fig. 29, Zones 2 and 3). It has been shown (182) that a shock compression ini-

tially raises only the translational energy of the molecules. Thus immediately following the detonation shock front, the gases are at a higher translational temperature than they would be at thermal equilibrium. If the rotational and vibrational relaxation times for the initial reactants at these conditions are longer than the induction time period, incomplete thermal equilibrium is obtained. The shocked reactant gases would be at a higher temperature, or thermodynamically "hotter," than they would be under equilibrium conditions. Assuming that the relative translational energy of the colliding molecules are responsible for the occurrence of the chemical reactions, the rate of chemical reaction would be increased. Therefore, the width of the reaction zone would be decreased, due to the higher non-equilibrium translational temperature. Through chemical reaction acts, the translational temperature following the induction period will then rise from the value attained in the induction zone to that characteristic of the Chapman-Jouguet state, while the internal energy of the product gases will increase largely through the production of species in higher than equilibrium internal energy levels. If equilibrium between the translational and various internal degrees of freedom in these species is not reached by the time the reaction zone terminates, the "effective" detonation temperature will be higher than that obtained on the basis of thermal equilibrium. A higher detonation temperature, of course, results in a higher detonation velocity, pressure and density. The proba-

bility of non-equilibration of external and internal degrees of freedom increases as the initial pressure, and thereby the detonation pressure and temperature, increases. This is because the reaction rate increases with temperature. Thereby the reaction zone width decreases, leaving less time for equilibrium to be established. In opposition to this "pressure" effect on thermodynamic equilibration is the fact that an increase in temperature also increases the rate constant for transfer of energy between the various degrees of freedom. It also increases the probability of collisions, thereby increasing the rate of establishment of equilibrium. Thus the overall influence of increased pressure on inhibiting the establishment of thermodynamic equilibrium is diminished by the accompanying increased temperature accelerating effects.

It should be pointed out that the probability of thermal non-equilibrium existing between the translational and internal degrees of freedom, in the product gases of the mixtures of concern in this investigation, appears to be rather small, especially at the lower pressure conditions. In the gaseous mixtures under investigation the temperature ranges predicted are such that only the translational, rotational and vibrational degrees of freedom are of importance. Electronic excitation which occurs above 5000°K is negligible. Studies have demonstrated that equilibration between translational and rotational energy requires about a hundred collisions at the most.

Equilibration of molecules with larger moments of inertia is faster than those with small moments of inertia; i. e.,  $\text{CO}_2$  equilibration is faster than  $\text{H}_2$  (40, 50, 137, 161, 182). Equilibrium with vibrational degrees of freedom is somewhat slower, but is accelerated strongly by rising temperature (287). Under the lower initial pressure conditions of the present experiments the collision frequency is about  $10^9 \text{ sec}^{-1}$  (182). Thus the rotational equilibration should be completed with  $10^{-7} \text{ sec.}$  or sooner and the vibrational equilibration slightly after (20, 48). Under the higher pressure and correspondingly higher temperature conditions, the relaxation times will be corresponding less (115, 161).

Results from the detonation experiments performed by Berets, Greene and Kistiakowsky (17) in stoichiometric hydrogen-oxygen mixtures admixed with argon (which has no internal degrees of freedom) at 1 atmosphere initial pressure, indicated that complete thermodynamic equilibrium was achieved in these mixtures within the time available in the detonation wave. Analysis by Fay (117) also comes to this same conclusion. (From results obtained by other investigators, the reaction zones in mixtures similar to those considered in this investigation have a duration somewhat less than 1 microsecond at an initial gas mixture pressure of 1 atmosphere (8, 17, 103, 120, 264)). It would appear, therefore, that sufficient

time is available for equilibration to be obtained of translational and all internal degrees of freedom for the species involved in the reactions, at least at the lower pressure conditions. The reaction zone width (and time duration) have been found to decrease rapidly with increase in initial pressure. It is possible, therefore, that insufficient time may be available for the gaseous species involved in some of the mixtures to reach thermodynamic equilibrium before termination of the reaction zone at the higher initial pressures considered in this investigation.

The effect of thermal non-equilibrium, insofar as stable detonation phenomena is concerned, would be to increase the detonation velocity, pressure and temperature. The effect possibly would be greatest at the higher pressures. If such non-equilibrium did exist and were taken into consideration in the theoretical calculations, it is apparent that theoretically calculated values of detonation velocity and pressure would be closer to the experimental values obtained at the higher pressures and somewhat farther away at the lower pressures considered. It is probable, therefore, that real gas effects, combined with possible thermal non-equilibrium effects in the product gases, could account for most of the deviation between theoretically calculated and experimentally determined values of detonation parameters at the higher pressure conditions.

## 6. Energy Losses Due to Non-Attainment of Chemical Equilibrium

The experimental detonation velocity, pressure, temperature and density may be lower than the theoretical Chapman-Jouguet values due to the fact that chemical equilibrium of one or more of the product species is not achieved before termination of the reaction zone at the Chapman-Jouguet point. If chemical equilibrium is not attained, the chemical energy available for support of the detonation wave propagation will be less than that which would be available if total chemical equilibrium were achieved. The magnitude of available chemical energy is dependent upon the rates at which the various chemical species involved in the reaction products approach equilibrium. These rates of equilibration are primarily dependent upon the reaction temperature. Other influences such as third-body effects due to additions of pure diluents or other additives will normally enhance the number of effective completed reactions. At the same time, however, they may lower the reaction temperature sufficiently so that the overall number of completed reactions are reduced. (These points will be discussed in more detail in a subsequent paragraph of this section when interpretation is made of the influence of the various additives considered in this investigation on the values of the detonation parameters).

Kistiakowsky and co-workers (48, 182) and others, from their

measurements of the density profile in detonation waves, have determined that a major portion of the available chemical energy release in a detonation wave occurs in the initial portion of the reaction zone immediately following shock front. Thereafter, it is maintained that the rate of energy release decreases at an increasing rate and equilibrium is approached asymptotically. It can readily be seen that if the reaction zone is terminated before one or more of the reactions involved reaches equilibrium that the energy decrement (normally exothermic) would not be available to support the detonation wave propagation. For example, if rarefaction waves moving from behind and from the lateral detonation tube walls, such as postulated by Kistiakowsky, et. al. (48, 176, 182) occur within the reaction zone thus effectively terminating it, and if equilibrium of some of the reactions has not been reached at this time, the rest of the spontaneous reaction will occur in the rarefaction wave. The energy released in the rarefaction wave will have no effect on the support of the detonation wave propagation because looked at from this region the detonation front propagates with supersonic velocity. If this is the case it would be expected that the experimental detonation velocities and pressures would be lower than those calculated on the basis of complete chemical equilibrium, since a portion of the energy is not utilized in the support of the wave propagation. The chemical energy loss, and therefore its influence on the values of the detonation parameters, however, should be relatively small under



usual detonation conditions. This is because, as pointed out previously, the majority of the available chemical energy is released almost immediately following the shock front. However, it is not improbable that the energy loss due to the deficiency in chemical energy addition is of the same order of magnitude as that due to transport dissipation. Therefore, it could have comparable effect on the values of the detonation parameters.

Just as with energy losses due to friction and transport, energy losses due to non-attainment of chemical equilibrium at the Chapman-Jouguet point decrease as the initial pressures ( and detonation pressure, density and temperature) increase. This, of course, is due primarily to the increase in reaction rates and the number of effective completed reactions at these conditions. Thus energy losses due to non-attainment of chemical equilibrium should be considered primarily a relatively low pressure phenomena. At high initial ( and final detonation pressures and temperatures) they are overshadowed, just as are friction and transport effects, by other influences; e. g. , real gas effects.

7. Deviations Due to Chemical Reaction in the Shock Front or In The Induction Zone.

If there is any chemical reaction taking place in the shock front of the detonation wave or in the induction zone, then at the termination

of these regions the temperature will be higher and the pressure lower than that for the case of a non-reacting shock wave and chemically passive induction zone. In essence this would mean that the peak pressure ("von Neumann spike") would be lower than the non-reacting shock peak pressure or the theoretical "von Neumann spike" peak pressure. In all probability, however, due to the very narrow width of the shock front and induction zone, it is extremely unlikely that sufficient time is available for any significant amount of chemical reaction to take under the initial conditions and in the mixtures considered in this investigation. Thus it is felt that any influences on the values of the detonation parameters due to chemical reaction taking place in the shock front or induction zone are small and undoubtedly negligible in comparison to the influence of some of the other effects discussed previously in this section.

#### 8. Discrepancies Due to Non-Planar and Multi-Dimensional Detonation Wave

Tilt or inclination of the shock front of a detonation wave should not cause any discrepancies between experimental and theoretical values of detonation parameters, (e. g., velocity and pressure) provided that during its propagation down the detonation tube the wave is steady and one-dimensional, the inclination angle remains constant, and the events occurring in and the characteristics of the reaction zone remain the same. If, however, the wave front is irregular or

curved (multi-dimensional) and changes erratically in orientation and/or chemical or physical behavior as the wave progresses down the tube, it would be expected that deviations would occur. Recent investigators (48, 79, 80, 91, 93, 119, 120, 159, 218, 219, 234, 238, 239) have found that at ambient initial gas-mixture pressures and above, with large diameter tubes, and in mixtures where the reaction zone thickness is small compared to the tube diameter, that the detonation wave is planar and macroscopically steady. However, it was found that at low sub-ambient pressure conditions where the wave thickness begins to approach the dimensions of the tube diameter, the wave appears to be non-uniform and far from steady in the reaction zone. Also the detonation front appears to be irregular, plane only on the average and changing erratically in orientation as it propagates down the detonation tube. This phenomena becomes increasingly accentuated as the initial pressure is decreased. Thus, at very low initial pressure conditions, apparently there is a very intimate coupling between shock front and the reaction zone; the wave is non-steady and non-uniform throughout the reaction zone; and the simple existing one-or-two-dimensional steady flow theories are not adequate to describe the detonation phenomenon under these circumstances.

As can be inferred from the above discussion, one need be concerned with the effects of detonation wave non-planarity and associ-

ated multi-dimensional effects, both space-and time-wise, only under conditions where the reaction zone width is approaching the dimensions of the container. Such a condition would prevail only in detonable mixtures at very low sub-ambient pressures, and possibly in mixtures with a considerable portion of diluent added at a somewhat higher initial pressure. Thus, the effect of these phenomena on the values of the detonation parameters is seen to be of possible consequence only at very low initial pressures, the effect probably being accelerated in mixtures containing large percentages of diluents. Any influence due to such effects decreases very rapidly with increase in initial gas mixture pressure ( and decrease in percent diluent ) ( 17, 18, 91, 119, 120, 234 ).

It is the opinion of this investigator that the influence on the values of the detonation parameters, e. g., detonation velocity and pressure, due to detonation wave non-planarity, irregular change in wave front orientation during propagation and non-steady and non-uniform characteristics of the reaction zone, is relatively small and probably negligible in comparison to other effects, under all initial conditions and in all mixtures considered in this study. Possible exceptions to this might be in the mixtures investigated at the lower range of initial pressures; i. e.,  $1/2$  and 1 atmospheres. The effects discussed above could very nicely account for the small differences in the values obtained for the average detonation wave

propagation rate between each ionization-probes intervals under these conditions (See Tables 13 through 24, Appendix IX).

From the analysis made in the previous paragraphs of this section, at the lower initial pressure conditions, it would be expected that the experimental detonation velocities and static pressures would be somewhat lower than the theoretically calculated idealized Chapman-Jouguet values, for all the mixtures considered in this investigation. It is the opinion of this investigator that energy losses primarily due to friction and transport and chemical energy deficiency, brought about by the non-attainment of chemical equilibrium of one or more species at the Chapman-Jouguet state, reasonably account for these discrepancies in the low initial gas-mixture pressure ranges tested. If corrections due to these losses were taken into consideration, the deviations between experimental and theoretical velocities and pressures at the lower initial pressure ranges would be decreased considerably. As a further consequence of this analysis, it is believed that connections due to these losses at high initial gas-mixture pressures are insignificant in comparison with real gas influences.

F. Influence of Additives on the Trend of Experimental Data and Deviations at Low Initial Pressures

As indicated previously, the values of the theoretically calculated

Chapman-Jouguet detonation velocity and pressure are decreased by the addition of chemically inert (i. e., helium or argon) or chemically reactive (i. e., carbon dioxide) additives to the "basic" mixture ( $2\text{H}_2 + \text{O}_2$ ). The decrease in each case was found to be proportional to the amount of additive included in the initial mixture. It was also seen that the experimental curves of detonation velocity and pressure follow the same general trend as the theoretical curves, but that the experimental values are somewhat lower in the lower initial pressure range and somewhat higher in the higher pressure range. It was seen also that the amount of deviation between theoretical and experimental values differs somewhat for similar amounts of different additives admixed with the basic mixture at the same initial conditions of pressure and temperature.

Previous paragraphs in this section have analyzed and discussed the reasons for these discrepancies at both the low and high initial pressure ranges. Also analyzed were the reasons for and comparison of the trends in these deviations at the higher pressure range due to the influence of various amounts of the different additives admixed with the "basic" mixture. In the following paragraphs analysis will be made of the influence of each of the different additives on the values of the experimental detonation velocity and pressure at the lower initial pressure conditions. At the same time a comparison

will be made of the influence of each different additive on the magnitude and the trend of the deviations between the experimental and theoretical values of these parameters under these conditions.

In order to make this analysis, it will be necessary to consider simultaneously for each system all of the different effects discussed in the previous portions of this section which were found to be important at the lower initial pressure conditions considered in this investigation. These effects primarily include influences due to reaction kinetics (e. g. reaction rates, three-body influences, reaction zone thickness), wall effects (e. g. , friction and heat conduction), and the acoustic velocity in the additive-mixture reaction products.

It has been seen that for like amounts of the theoretically thermodynamically and chemically identical inerts (helium or argon) added to the basic mixture, the theoretically calculated thermodynamic and state properties were identical. It has been shown also that the hydrodynamic - dependent properties, e. g. , the Chapman-Jouguet velocity, were proportional to the reciprocal of the square root of the final product density. This is because for the same amount of inert gas added, the detonation temperature ( $T''$ ), specific heat ratio ( $\gamma$ ) and density ratio ( $\rho''/\rho'$ ) are the same.

The theoretical Chapman-Jouguet detonation velocities in the carbon dioxide-additive mixtures also were found to conform in general to the square-root density rule. However, in all cases they were somewhat lower. In addition, the thermodynamic and state properties for the carbon dioxide-additive mixtures were lower than with comparable percentages of the helium-or argon-additive mixtures. These differences were due to the differences in thermodynamic properties of carbon dioxide and to the participation of carbon dioxide in the product chemical equilibrium. In the real situation at low initial gas-mixture pressures, the effects previously discussed produce deviations between the values of the theoretical and experimental detonation velocities and pressures. They also produce differences in the magnitudes of these deviations for the different additives at the same initial conditions.

The differences in the magnitudes of energy losses due to "wall effects" will be considered first. As indicated previously, these losses are due primarily to friction (viscous) and heat conduction (thermal transport) to the cold tube walls in the reaction zone of the detonation wave. The friction coefficients for all gases are about equal. Thus, to the greatest degree wall losses can be directly related to the thermal conductivity of the gaseous products. Further, for the same "basic" gaseous mixture (i. e. stoichiometric hydrogen-oxygen admixed with equal amounts of different additives



at the same initial pressure and temperature, the heat losses will be proportional to the thermal conductivities of the additives.

The thermal conductivity is inversely proportional to the molecular weight and complexity of a particular specie. The thermal conductivity of helium is approximately ten times that of argon or carbon dioxide. That of argon is somewhat higher than that of carbon dioxide (3, 220). Thus the mixtures containing the lighter additives should give greater heat losses per unit width of reaction zone than the mixtures containing like amounts of heavier additives. That is, helium-additive mixtures should give greater heat losses than the corresponding argon-additive mixtures; and the argon-additive mixtures should give greater heat losses than the corresponding carbon dioxide-additive mixtures.

From the above analysis, it can be seen that the magnitude of the energy loss due to wall effects for any of the additive mixtures considered is intimately associated with the "effective" width or thickness of the detonation reaction zone, and possibly the boundary layer. The "effective" reaction zone width is primarily a function of the rates at which the reaction products approach equilibrium. These are controlled to the greatest extent by the reaction temperature and, to a much smaller degree, by the pressure. Extraneous effects, e. g., third-body effects, also enter into the picture since

they affect the rate of effective completed reactions, as well as the reaction temperature and pressure. Also the acoustic velocity in the burned gases could be of significant influence in determining the "effective" reaction zone width.

For the ideal case, where no losses are considered, the reaction rates and therefore the reaction zone widths for the chemically and thermodynamically identical helium-or argon-additive mixtures at the same initial conditions should be identical since their reaction temperatures and pressures are identical. For the corresponding carbon dioxide-additive mixtures under the same conditions, the reaction rates should be lower and the reaction zone width larger due to the lower theoretical detonation temperature and pressure involved. In the real case, these ideal reaction rates and reaction zone widths may change appreciably, depending on the additive involved.

In the mixtures considered in this investigation, the additives admixed with the basic mixture ( $2\text{H}_2 + \text{O}_2$ ) act as third-body agents. Each of the additives is different in its degree of effectiveness in absorbing the excess kinetic energy of the colliding reacting species and thereby increasing rate of effective completed reactions. The heavier and more complex molecules are normally the most effective third-body agents, being able to "absorb" better the excess energy

of the colliding atoms by distributing it among their various degrees of freedom. Lewis and von Elbe (202) indicate that carbon dioxide is approximately seven times as effective as argon and four times as effective as helium, and that helium is about twice as effective as argon in their effectiveness as third-body agents.

In addition to the third-body effect discussed above which tends to increase the rate of effective reactions, it is necessary to consider the diluent effect of the additive on the reactant temperature and pressure in order to determine its overall effect on the reaction rate and reaction zone width. The additives considered in this investigation contribute nothing to the exothermic energy release utilized to support the detonation wave propagation. Rather, the available energy per unit mass of product mixture is reduced by the dilution effect of the additive. Thus, as been previously pointed out, the detonation velocity, pressure, temperature and density are reduced. Since the reaction rates are very strongly dependent upon the temperature, and to a lesser degree upon the pressure ( or density), it is seen that the overall reaction rates will be decreased ( and the reaction zone width increased) due to the dilution effect of the additive.

A quantitative determination of the net influence of these two counter-acting effects on the rate of effective reactions would be very

difficult to determine with available experimental information. If it is assumed that the temperature decrease due to the dilution effect of the additive has greater influence over the reaction rate than the third-body effect, the reaction rates for the basic mixture admixed with like amounts of additives at the same initial conditions should be lowest (and the reaction zone width largest) for the carbon-dioxide additive mixtures, next lowest for probably the argon-additive, and highest for the helium-additive mixtures. This condition is not too improbable, especially in mixtures containing large amounts of diluents or initially at low gas-mixture pressures where the temperatures can become relatively low.

In addition to the above effects, the influence due to the differences in the acoustic velocities in the product gases of the different additive mixtures must be considered before making any final comparisons of the overall influence of the different additives on the values of the experimental detonation parameters. It has been pointed out previously that only the spontaneous energy evolution occurring in the reaction zone of the detonation wave has an effect on the propagation of the detonation wave. Also any reactions which may continue on in the expansion or rarefaction wave trailing the Chapman-Jouguet region have no influence on the detonation velocity or pressure. The velocities of the rarefaction waves moving from behind and also of

the rarefaction waves from the tube walls (as postulated by Kistiakowsky) are functions of the acoustic velocity in the mixture. Thus the time scale for completion of the reaction processes in the wave is dependent upon this hydrodynamic influence. Due to this acoustic velocity influence it would be expected that the "effective" reaction zone width, would be a function of the molecular weight and temperature of the reaction products. It should be smaller in mixtures diluted with the higher molecular weight species, i. e., helium-smallest, larger in argon- and largest in carbon dioxide-additive mixtures. As a consequence of shortening the reaction zone, the time available for completion of reaction is decreased. Thus, less energy would be available for support of the detonation wave. Therefore a lower reaction temperature, pressure and velocity should result. The decrease due to the influence of acoustic velocity should be most pronounced in the helium-additive mixtures, of less consequence in the argon-additive mixtures, and of least effect in the carbon dioxide-additive mixtures.

A comparison will now be made of the accumulative influence of all the effects discussed and analyzed in the previous paragraphs on the magnitudes and trends in the deviations between experimental and theoretical detonation velocities and static pressures obtained for the mixtures considered in this investigation at the lower initial pressure range. A comparison will be made first between the helium-additive

and the corresponding argon-additive mixtures. This comparison will then be extended to encompass the corresponding carbon-dioxide additive mixtures and the pure stoichiometric (basic) hydrogen-oxygen mixtures.

Because of the higher acoustic velocities in the helium-additive mixture reaction products, it would be expected that the time available for the various chemical reactions involved to reach equilibrium would be less for the lighter helium-additive than for the corresponding argon-additive mixtures. Thus, a smaller "effective" reaction zone width would be obtained in the helium-additive than in the argon-additive mixtures. As a consequence of the decrease in "effective" reaction zone width, the chemical energy available for support of the detonation wave propagation should be decreased more in the helium-additive than in the corresponding argon-additive mixtures. The three-body effect acts to increase the amount of available energy in the helium-additive mixtures compared to that in the argon-additive mixtures. However, the influence of the third-body effect is roughly the same in these mixtures. In any event it probably is relatively small in comparison to the dilution effect of the additive (i. e., lowered temperature and reaction rate) and to the acoustic velocity effect.

In addition to the greater chemical energy losses due to non-achievement of chemical equilibrium at the termination of the Chapman-Jouguet plane, the energy losses due to thermal transport and other wall effects are much larger per unit width of reaction zone in the helium-additive mixtures. Thus, even with a somewhat smaller reaction zone width the total energy losses due to wall effects should be larger in the helium-additive than in the corresponding argon-additive mixtures at low initial gas-mixture pressures.

From the above analysis it is seen that the energy actually available for support of the detonation wave propagation is less in the helium-additive than in the corresponding argon-additive mixtures. It would be expected then that the experimental detonation velocities and pressures would be lower, and the differences between the experimental and theoretical detonation velocities and pressures (deficits) higher in the helium-additive mixtures than in the corresponding argon-additive mixtures at low initial gas-mixture pressures.

The theoretical speed of sound in the carbon dioxide-additive mixtures is somewhat lower than that in the corresponding argon-additive mixtures and appreciably lower than that in the corresponding helium-additive mixtures. Because of this, it would be expected that the time available for chemical reaction would be greater. There-

fore the "effective" reaction zone width for the carbon dioxide-additive mixtures would be somewhat larger than that in the corresponding helium-additive mixtures. Since the reaction temperature in the carbon-dioxide additive mixtures is considerably lower than that in either the corresponding argon-additive or helium-additive mixtures, the rates of chemical reaction will decrease appreciably. Thus even though the reaction zone width is relatively larger, the amount of energy available at the termination of the Chapman-Jouguet plane might be considerably less for the carbon dioxide-additive mixtures than for the corresponding argon-additive or helium-additive mixtures. The third-body effect of carbon dioxide acts to enhance the rate of liberation of chemical energy. However, no doubt this effect is overshadowed to a major extent by its greater dilution effect and consequent reduction of the reaction temperature, pressure and reaction rates. The energy losses due to heat losses to the tube walls should be roughly equal for the carbon dioxide-additive and the corresponding argon-additive mixtures, and probably somewhat greater for the helium-additive mixtures.

From the discussion presented above, it is probable that the overall decrease in available energy for the carbon dioxide-additive mixtures due to chemical energy and thermal losses are greater than those in the corresponding argon-additive mixtures. It is quite possible also that the energy losses in the carbon-dioxide additive



mixtures are greater than those in the corresponding helium-additive mixtures. In support of this contention, it was observed during the experimental investigation that some of the carbon dioxide-additive mixtures at the lower initial pressures could not support a steady detonation and sometimes not even a normal deflagration. Also it was observed that the mixtures capable of detonating were more difficult to ignite and required longer induction distances before stabilization than the corresponding helium-additive or argon-additive mixtures.

From the above analysis it would not be unreasonable to expect that the velocity and static pressure deficits at low initial pressures in the carbon dioxide-additive mixtures would be greater than those in helium-additive or in the argon-additive mixtures. Thus, in the lower initial pressure range, it would be expected that the greatest deviation (deficits) between the experimental and theoretical detonation velocities and pressures would be in the carbon dioxide-additive mixtures, somewhat smaller deviations in the corresponding helium-additive mixtures, and smaller deviations yet in the argon-additive mixtures.

It would be expected that energy losses would be involved also in the pure stoichiometric hydrogen-oxygen (basic) mixtures which would reduce the effective amount of energy available for wave

propagation. Thus, as in the various additive mixtures discussed, it would be expected that the experimental detonation velocities and pressures at the low initial pressures would be lower than the corresponding theoretical Chapman-Jouguet values. In the pure stoichiometric mixtures, however, there is no dilution effect. Thus the reaction temperature and reaction rates should be higher and the reaction zone width smaller. Therefore, the losses due to thermal transport and other wall effects should be smaller in the pure (basic) mixture than in any of the additive mixtures considered in this investigation. It can be seen then that the energy available per unit mass of mixture for propagation of the detonation wave, even though it is lower than that which is theoretically possible, is larger for the pure stoichiometric hydrogen-oxygen mixtures than for any of the additive-mixtures considered in this investigation. Thus a deficit in detonation velocity and pressure should be expected to be of smaller magnitudes than those of any of the additive mixtures considered at the same initial pressure and temperature.

It would be expected further that the velocity and pressure deficits at the lower initial pressure range for all mixtures considered would increase progressively as the initial pressure decreases and/or the additive composition increases. This is because the energy losses due to the effects discussed in the previous paragraphs increase under the conditions.

From the tabulations and plots of the experimental detonation velocities and static pressures, ( Figs 35 through 42 and Tables 13 through 24, Appendix IX) it can be seen that the magnitudes of the deviation of the experimental and theoretical data for the different mixtures considered at low initial pressures, as well as the trend of these deviations with initial pressures and percentage additive, are in quite reasonable accord with those predicted by the analysis presented in the previous paragraphs.

The energy losses due to the effects discussed in the previous paragraphs are cumulative. That is, the energy losses due to wall effects cause a decrease in the detonation temperature, pressure and velocity and thus also lower the shock front temperature. The decrease in shock-front temperature in turn lowers the reaction rates according to Arrhenius' law. This in turn increases the width of the reaction zone and hence increases the heat loss. If the rate of production of useful energy is not sufficient to overcome these losses, the detonation wave cannot be sustained. (In all probability this is the predominant reason why several of the carbon dioxide-and other additive mixtures investigated in this study would not support a steady detonation wave.) On the other hand if the cumulative losses are less than the rate of production of useful energy, a steady detonation wave will be established.

Kirkwood and Wood (174) have shown thermodynamic (chemical equilibrium) is not an essential requirement for the establishment of a stable detonation wave. Peek and Thrap (248, 249) and Kistiakowsky and co-workers (17, 179, 180, 186) have extended the work of Kirkwood and Wood (174) and have shown that the analysis also holds if thermal equilibrium has not been achieved. Due to the energy losses involved, because of lack of thermal and chemical equilibrium and other effects previously discussed, the available useful energy is below the energy level required for the propagation of the ideal Chapman-Jouguet wave. Thus, the detonation velocity, pressure and temperature will be less than those based on complete equilibrium and no energy losses. Under these real conditions the Chapman-Jouguet (C-J) plane should no longer be regarded as the point of complete chemical and thermal equilibrium, as it is for the ideal detonation wave. Rather, the Chapman-Jouguet condition, i. e., the equality of detonation with the sum of acoustic and material velocities ( $D = u'' + a''$ ), should be modified so that it holds for the plane in which the energy required to propagate the wave, the useful energy, is just balanced by its losses. The detonation waves in these mixtures correspond to the so-called "sub-ideal" Chapman-Jouguet detonation waves of Brinkley and Richardson (39). For these cases the Hugoniot curve defining the thermodynamic state of the burned gases would not be that corresponding to complete attainment of thermal and chemical equilibrium (i. e.,  $N = 1$ , Fig. 1). Rather, it would correspond to some Hugoniot

curve lying between the non-reactive shock Hugoniot (i. e.,  $N=O$ , Fig 1) and the Hugoniot for complete equilibrium, the actual Hugoniot being determined by the magnitude of the energy losses involved. The occurrence of this wave, of course, is associated primarily with low initial pressure and/or quite highly diluted (low energy release) mixtures where the energy losses due to thermal and chemical energy deficiencies may be of consequence. Therefore, further discussion in this section pertaining to the sub-ideal Chapman-Jouguet detonation wave will be confined to lower initial pressure detonations.

From a comparison of the theoretical and experimental detonation velocities and pressures obtained in the mixtures investigated, (See Tables 13 through 24, Appendix IX) it is the opinion of this investigator that the simplified thermohydrodynamic theory gives a correct description of the detonation wave and can be used with confidence to predict the detonation parameters in the (basic) stoichiometric hydrogen-oxygen mixtures down to the lowest initial pressures considered; i. e., 1/2 atmosphere. Therefore, it is felt that the detonations in these mixtures at the low initial pressure range can reasonably be considered to be ideal Chapman-Jouguet detonation waves.

For the remainder of the mixtures investigated; i. e., stoichiometric hydrogen-oxygen admixed with helium, argon or carbon dioxide, as indicated previously, from a practical viewpoint it is felt that the

idealized thermohydrodynamic theory also reasonably predicts the detonation velocities and static pressures, for those mixtures capable of supporting a detonation, down to the lowest initial pressures considered in this investigation; i. e.,  $1/2$  atmosphere. However, the predicted values of detonation velocity and pressure are not as close to the experimental values as those of the pure stoichiometric hydrogen-oxygen mixtures. Nevertheless, it is still believed that the idealized thermohydrodynamic theory can be used with a good degree of confidence for these mixtures, even though in a number of additive mixtures, especially those where relatively large amounts of additive are present, the detonations from an academic viewpoint probably should be considered to be sub-ideal.

For example, all helium-additive and argon-additive mixtures containing above 10% additive and all carbon dioxide-additive mixtures containing above 4% additive at initial pressures between  $2-1/2$  to 5 atmospheres and below were found either to have fairly large velocity and pressure deficits (See Tables 13 through 24, Appendix IX) to have relatively long predetonation lengths (See Figs. 43 through 47), or to be incapable of supporting a detonation at all. It is quite possible that the detonation waves should be considered as subideal in those relatively high-percentage additive mixtures at the lower initial pressures where stable detonation is attained or is being approached. Certainly in these mixtures (as well as in those mixtures

incapable of supporting a detonation) energy losses play an important part.

It should be emphasized, however, that even in mixtures investigated where there is quite close agreement between experimental and theoretical detonation velocity, it cannot be inferred that chemical and/or thermal equilibrium has been rigorously established in the Chapman-Jouguet plane of the detonation wave, especially at the lower initial pressure conditions. Indeed, there is no cause to believe that in these mixtures such equilibria are exactly attained. It is well known, for example, that in mixtures similar to those investigated the formation of water at low initial pressures is very far from complete due to the high temperatures involved. Calculations carried by Berets, et. al. (17) for the stoichiometric hydrogen-oxygen mixture, assuming off-equilibrium concentrations of water formation, gave a detonation velocity in very close agreement with that assuming an equilibrium composition of water. Also calculations for the same mixture made by Lewis and Friauf (195) and Scoriah (281) neglecting some of the dissociation reactions involved and using somewhat different heat capacities, differ only slightly from the calculations of Berets, et. al. (17) and the data reported in this investigation. This shows that some quantities such as detonation velocity are comparatively insensitive to the precise reaction equations, equilibria or product composition assumed.

Therefore good agreement of calculated and experimental velocities is no proof that chemical and thermal equilibrium is accurately established in the detonation wave. There can be seemingly perfect agreement of experiment and theory without the theory being exact in detail.

Thus, all that can be said with reasonable assurance, for these mixtures investigated where good agreement was observed between experimental and theoretical velocities, is that the Chapman-Jouguet theory applies rigorously to these mixtures. However, it applies only in the sense that the detonation velocity may be set equal to the sum of the acoustic and mass velocity of the equilibrium mixture, making it the lowest velocity consistent with the Rankine-Hugoniot conditions for the particular mixture.

In order to prove conclusively that complete thermal and chemical equilibria are achieved at the Chapman-Jouguet plane, it would be necessary to have knowledge of the relaxation times and reaction rates of the reaction species involved, the reaction zone width, the heat losses due to wall effects, real gas effects, and influences due to all the other effects discussed in the previous paragraphs of this section. Obviously, this would be a very difficult if not impossible task to accomplish. The best that could be hoped for would be to approach the true answer. This was essentially what was envisioned



in this investigation when attempts were made to measure precisely detonation velocity and static pressures simultaneously. Unfortunately, as was pointed out previously, the pressure measurements obtained in this investigation were not precise enough to permit quantitative assessment of the attainment of equilibria in the mixtures investigated.

## VI CONCLUSIONS

The measured and theoretically calculated Chapman-Jouguet detonation velocities and static pressures were in reasonable agreement for all mixtures and at all initial pressure conditions considered where steady-state fully-developed detonations were attained. Reproducibility of experimental velocities was on the order of  $\pm 1/2$  percent. The highly idealized Chapman-Jouguet thermodynamic theory of detonation is valid and can be used with confidence to predict realistic values of detonation velocities over an initial pressure range of  $1/2$  to 50 atmospheres and to predict detonation static pressures over an initial pressure range of 1 to 5 atmospheres, in all the gaseous mixtures considered.

The experimental detonation velocities in all mixtures investigated were somewhat lower than the theoretical values at the lower initial pressure range. The agreement was poorest for the stoichiometric hydrogen-oxygen-carbon dioxide mixtures and best for the pure stoichiometric hydrogen-oxygen mixture. The deviations increased as the initial pressure decreased and the additive concentration increased. At the lower initial pressures and the higher additive concentrations, the small disagreements between experimental and predicted velocities were probably the result of oversimplifications in the idealized

theoretical model; e. g. , the assumption of a planar discontinuity, chemical and thermal equilibrium, and no heat ( thermal transport) or momentum ( viscous) dissipation to the walls. Inconsistencies at the lowest initial pressures and in the most dilute mixtures were probably due to the detonation tube not being sufficiently long to permit achievement of steady-state fully developed detonation. The erratic and non-reproducible wave velocity measurements were probably due to the non-planarity and non-repeatability and general unstable make-up of the combustion waves in the detonation build-up region. These deviations should not be interpreted as a contradiction of the thermohydrodynamic detonation theory.

At the higher initial pressures the experimental detonation velocities were somewhat higher than the theoretical values. The deviations increased as the initial pressure increased. The disagreement was small and was probably due principally to the idealized properties and idealized caloric and thermal equations of state necessarily used in the theoretical computations. Without high pressure values for the properties and real gas equations of state, the discrepancies can only be shown to be reasonable and not necessarily due to defects in the Chapman-Jouguet theory.

No quantitative conclusions can be made about whether complete chemical and/or thermal equilibrium in the Chapman-Jou-

guet plane was established, or whether the "frozen" or "equilibrium" product gas sound speed is the most correct in the real gas situation. The detonation velocity was only slightly dependent upon initial pressure but was critically dependent on mixture composition. The experimental detonation static pressures followed the same general trend as the velocities. The theoretical detonation and shock wave pressures and temperatures increased linearly with initial pressure and were relatively independent of mixture composition. Detonation and shock wave pressures and temperatures should be seriously considered in the design of equipment subject to detonation. Computed detonation and normal shock wave pressures and temperatures based on the idealized thermohydrodynamic theory are adequate as a first-order guide.

No evidence was obtained of the "von Neumann spike" or of an induction zone immediately following the "spike." Also, no quantitative conclusions can be made pertaining to the true model of the detonation wave structure. The pressure measuring system used did not have sufficient time resolution to detect such highly transient phenomena, if they do indeed exist. The pressure measuring system was not entirely satisfactory. The experimental pressure data presented should be considered as qualitative only due to the uncertainty associated with the pressure measurements,  $\pm 20$  to  $\pm 60$  psi. With some additional modifications, i. e., improving the characteristic

of the pressure transducer shock mount and the electrometer tube, very accurate pressure measurements could have been obtained at rise times of about 0.5 microseconds. In all probability, however, the response would still not be rapid enough to sense the very steep shock front ( "von Neumann spike" ), the induction zone immediately following the shock front, or even the reaction zone, as stipulated by the modified NDZ model of detonation, except possibly at very low initial pressures and/or in highly diluted detonable mixtures.

Additives retarded the rate of attainment of steady fully-developed detonation in hydrogen-oxygen mixtures. The stabilization rate increased with increase in initial pressure and with decrease in additive concentration. The rates appeared to be closely associated with the predetonation lengths, the deviations between theoretical and experimental values of detonation parameters, and the detonation limits. Addition of carbon dioxide had the greatest influence and argon the least on these quantities and on the mechanism of detonation in the gaseous mixtures considered.

## APPENDIX I

### POSTULATED MODEL OF DETONATION

The model of the stable detonation wave structure which is the basis for the theoretical analysis performed in this investigation, is essentially the same as that postulated by von Neumann ( 304 ), Döring ( 87, 88 ) and Zeldovich ( 320, 321, 322 ), but modified by the inclusion of an "induction zone" between the shock front and the reaction zone, as hypothesized by Kistiakowsky ( 176 ), Lewis and von Elbe ( 203 ), Finklestein and Gamov ( 123 ), Mallory and Jacobs ( 215 ), and others. ( See Literature Review, Section IIE-1 for details ). This model is felt by the author to be a substantially correct simulation of the actual physical phenomenon. The qualitative features of the detonation wave based on the postulated model are shown in Fig. 28. The detonation wave is considered to be a one-dimensional plane steady-state composite wave propagating through a homogenous detonable gaseous mixture in a constant-area duct. Dissipating effects of diffusion, friction and heat-transfer ( wall effects ) in the detonation wave, etc. , are neglected. ( This assumption is believed justified because the molecular transports are much slower than the mass propagation rates produced by detonation waves ). The first part of the detonation wave ( the "von Neumann spike" ) is considered to be a non-reactive shock wave of a few mean paths thickness propagating through the chemically unreacted gaseous mixture at the velocity thermodynamically calculated for the stable

detonation wave. The pressure, temperature and density are assumed to increase and the velocity to decrease essentially discontinuously across the shock front or "spike" (Point A in Fig. 28 and Point G' in Fig. 1). It is considered that chemical reaction of the detonable mixture is initiated by the shock wave. The second part of the detonation wave is an induction zone (Region A-B, Fig. 28) where little or no chemical reaction occurs, where the system attains thermal equilibrium and where the pressure, temperature, density and mass velocities have negligible gradients. Following the induction zone is a steady-state reaction zone (Region B-C in Fig. 28) where thermal energy released by the chemical reactions is added to the subsonic flow behind the normal shock wave and induction zone, resulting in a gradual decrease in pressure and density and an increase in temperature and velocity as the reactions progress towards thermodynamic and chemical equilibrium. The reaction zone is considered to terminate at the classical Chapman-Jouguet point on the equilibrium Hugoniot (Point C, Fig. 28 and Point D, Fig. 1) where the local flow velocity plus the equilibrium sound speed equals the detonation velocity, and chemical and thermodynamic equilibrium exist. The state properties associated with the classical Chapman-Jouguet condition; i. e., pressure, temperature, density, composition, and velocity are considered to remain essentially constant in the region immediately following the Chapman-Jouguet point (Region C-D, Fig. 28). This region shall be

designated as the Chapman-Jouguet region or plane. Following and closely coupled to the Chapman-Jouguet plane is an unsteady-state regime of an isentropic rarefaction or Taylor wave (Region D-E, Fig. 28) in which the pressure, density, forward velocity and temperature of the burned gases fall gradually until they finally come to rest (Point E, Fig. 28). The depth of the Chapman-Jouguet region (Region C-D, Fig. 28) is dependent upon the time it takes for the rarefaction wave to interact with the Chapman-Jouguet region. (See Fig. 28, Region D-E).

The distance between the front of the non-reacting shock wave and the point where the subsonic flow behind the wave has become sonic, i. e., the Chapman-Jouguet point, is considered to represent the thickness of the detonation wave (Region A-C, Fig. 28). The wave thickness depends on the rate of chemical reactions, and it is larger for lower reaction rates. The steady Chapman-Jouguet detonation velocity is determined solely by the equilibrium conditions in the wave and is not affected by the rates of chemical reactions as long as losses are disregarded, i. e., all energy liberated by chemical reaction is considered to support the propagation of the shock front.

The detonation process proposed by von Neumann, Döring and Zeldovich, as represented on the Rankine-Hugoniot diagram, is discussed



in detail in the Literature Review, Section II-E1. Theoretical equations obtained on the basis of the postulated model are discussed in Appendix III.

## APPENDIX II

### THE RANKINE-HUGONIOT RELATIONSHIPS AND CURVE

For a steady plane flow devoid of transport effects and other losses, the conservation relationships of mass, momentum and energy, applied to shock waves with energy addition (detonation waves), relating the initial and final states of the detonable mixture; i. e., before and after the passage of the detonation wave, for a specified amount of energy addition, may be written without consideration of the path by which the change takes place. Assuming a coordinate system moving with the reaction front (See Fig. 29, Standing Detonation Wave Reference System.), the equations of conservation take the following form:

$$\rho' u' = \rho'' u'' \quad (\text{Mass}) \quad (\text{AII-1})$$

$$p' + \rho' (u')^2 = p'' + \rho'' (u'')^2 \quad (\text{Momentum}) \quad (\text{AII-2})$$

$$h' + 1/2 (u')^2 = h'' + 1/2 (u'')^2 \quad (\text{Energy}) \quad (\text{AII-3})$$

The single primes and double primes denote, respectively, the state of the unburned and burnt gases. Eliminating the velocity terms between equations (AII-1), (AII-2), and (AII-3), yields the (Rankine-) Hugoniot equation:

$$h = (h'' - h') = 1/2 \frac{p'}{\rho'} \left( \frac{\rho''}{\rho'} - 1 \right) \left( 1 + \frac{\rho'}{\rho''} \right) \quad (\text{AII-4})$$

Eq. AII-4 for an infinitesimally weak shock ( $p'' = p' + dp$ ;  $\frac{1}{\rho''} = \frac{1}{\rho'} + \frac{1}{\rho}$ ) reduces to the isentropic  $dh = Cp dT = dp/\rho$  (AII-5)

This follows from the first law of thermodynamics when  $dq$ , the amount of heat occurring during the process, is set equal to zero.

Combining equation (AII-4) with the ideal gas equation of state applied to the initial mixture,

$$\frac{p'}{\rho'} = \frac{RT}{m'} \quad (\text{AII-6})$$

gives the (Rankine-) Hugoniot energy equation as a function of  $p$  and  $\rho$ :

$$(h'' - h') \frac{m'}{RT} = \frac{1}{2} \left( \frac{p''}{p'} - 1 \right) \left( \frac{\rho'}{\rho''} + 1 \right) \quad (\text{AII-7})$$

Eq. (AII-7) is known as the (Rankine-) Hugoniot equation for various magnitudes of absolute enthalpy. It describes a hyperbola in the  $(p, v$  or  $p, \rho^{-1})$  plane, depending only upon the initial thermodynamic state (but not upon the initial velocity). The  $p$ - $v$  curve is the well-known "dynamic adiabatic" of Hugoniot, and it is the focus of points describing all possible states of the burned or detonated gas for each prescribed initial condition compatible with the conservation equations. A schematic plot of several of the Hugoniot hyperbola is represented in Figure 1, for fixed initial conditions  $(p', \rho^{-1})$  and varying magnitudes of absolute enthalpy, i. e., successive degrees of completion of the reaction or fraction of fresh gas reacted. The curve  $N=0$  corresponds to a pure shock wave with no chemical reaction. The  $N=1$  curve corresponds to complete reaction. The intermediate curves correspond to partial completion of reaction.

For a given upstream thermodynamic state and velocity (initial condition), the mass and momentum relationships (Eqs. AII-1 and AII-2) relate the pressure and density:

$$p'' - p' = (\rho' u')^2 \left[ \frac{1}{\rho'} - \frac{1}{\rho''} \right] \quad (\text{AII-8})$$

$$\text{or } (D \rho')^2 = (\rho' u)^2 = -(\rho'' u'') = -\left[\frac{p'' - p'}{(1/\rho'') - (1/\rho')}\right] \quad (\text{AII-9})$$

Eq. (AII-8) or (AII-9) is a straight line (Rayleigh line) in the  $(p, \rho^{-1})$  plane extending from the initial conditions and intersecting the detonation branch of the Hugoniot curve at two points in general. The slope of this line corresponds to the square of the mass flow per unit area and is a function of the velocity. The Rayleigh line contains all possible states of the gas from unburned ( $N = 0$ ) to completely reacted ( $N = 1$ ), and it corresponds to subsonic frictionless flow with heat addition.

For the region AB (not including the end points),  $p'' > p'$  and  $(\frac{1}{\rho''}) > (\frac{1}{\rho'})$  and it follows from Eq. (AII-9) that  $u''$  is imaginary. Thus the region AB does not correspond to physically reliable processes. The upper branch of the Hugoniot curve, ADF, represents detonation combustion; BCQ represents deflagration combustion. (Since this investigation involves consideration of detonation only, the deflagration branch will not be involved to any great extent in subsequent discussion). Point A corresponds to constant-volume detonation for which  $(\frac{1}{\rho'}) = (\frac{1}{\rho''})$ , and thus from Eq. (AII-8),  $u' = u'' = 0$ . Point B represents constant-pressure deflagration for which from Eq. (AII-9)  $u' = u'' = 0$ . Both points A and B correspond to limiting cases which have never been observed (110, 215, 250). In a neutral gas, i. e., no heat addition and no change in composition, points A and B would merge with A'.

For detonations  $p'' > p'$  and  $\left(\frac{1}{\rho''}\right) < \left(\frac{1}{\rho'}\right)$ ,  
 also from Eq. (AII-1):  $u'' - u' = -\left(\frac{p'' - p'}{\rho' u'}\right)$   
 i. e., a detonation wave retards the burnt gas.

The detonation and deflagration branches of the Hugoniot curve can be further characterized (68) as follows (See Fig. 1, Curve ADF.):

Region DF	Strong detonation	M' Supersonic	M'' Subsonic
Region AD	Weak detonation	M' Supersonic	M'' Supersonic
Point D	C-J Detonation	M' Supersonic	M'' Sonic
Region QC	Strong deflagration	M' Subsonic	M'' Supersonic
Region CB	Weak deflagration	M' Subsonic	M'' Subsonic
Point C	C-J deflagration	M' Subsonic	M'' Sonic

It is generally believed that weak detonation (See Region AD, Fig. 1) cannot occur for chemical reactions because the rates of reactions are not sufficiently rapid to maintain the detonation wave (88, 304, 320).

Brinkley and Richardson (39) and others have ruled out weak detonations on the basis that they violate the Second Law of Thermodynamics. Thus the only possible solutions correspond to the Chapman-Jouguet (C-J) detonation or to strong detonations. For the Chapman-Jouguet condition, the Rayleigh line (Eq. AII-9) is tangent to the Hugoniot curve (Point D, Fig. 1). It should be noted

that the singular solution of the Chapman-Jouguet condition is the only one always detected in flame tubes and shock tubes where the reacting gases are initially at rest. The present investigation is concerned only with the Chapman-Jouguet type detonation. Thus the possibility of attaining stable strong detonation (non-Chapman-Jouguet detonation) will not be discussed here.

### APPENDIX III

#### DERIVATION OF EQUATIONS FOR THE CALCULATION OF DETONATION PARAMETERS

##### A. General

The structure of the detonation wave, according to the model postulated in Appendix I of this dissertation can also be represented as shown in Fig. 29. In this representation the detonation wave is considered to be a zone which is steady in a coordinate system at rest in the shock front, and all velocities are taken relative to the detonation wave; i. e. , a standing wave coordinate system. In this system the detonation wave has zero velocity, the unburned gases enter the wave with velocity  $u'$ , (the detonation velocity) and the detonation products of combustion leave the wave with velocity  $u''$ . This system corresponds to the physical situation of the wave front moving into the stationary unburned gas with velocity  $u'$  and the detonation products immediately behind the wave front moving towards the unburned gas with a velocity  $(u' - u'') = W$ .

The initial state of the gas ( zone 1 ) is denoted by a single prime. The conditions immediately behind the non-reacting normal shock are identified by the subscript "NS. " The conditions in the induction zone ( zone 2 ) are assumed to be the same as those immediately behind the normal shock and thus are also identified by the subscript "NS. " The zone in which the chemical reaction takes place ( zone 3 ) is denoted by the subscript "rz. " The final state of the detonation products

at the Chapman-Jouguet point ( zone 4) is designated by a double prime. The gas immediately behind the shock wave and in the induction zone ( zone 2) is assumed to have the same composition as the initial gas ( zone 1); i. e., no chemical reactions occur. It is assumed further that in the induction zone equilibration of the vibrational degrees of freedom in the molecules in the gas mixture is completed; i. e., constant specific heats. The detonation products at the Chapman-Jouguet point ( zone 4) are assumed to be in a state of complete thermodynamic and chemical equilibrium. The theoretical analysis and calculations in this report will be limited to the non-reacting shock wave ( zone 2) and to the stable Chapman-Jouguet region ( zone 4). The derivations pertaining to the Chapman-Jouguet region will be treated first.

#### B. Chapman-Jouguet Detonation Parameters

Considering the Chapman-Jouguet plane as the boundary between the states before and after the reaction, the system includes the following unknown properties:  $T''$ ,  $p''$ ,  $p_i''$  ( $i = 1, 2, 3 \dots N''$ ),  $\rho''$ ,  $n''$ ,  $u''$ ,  $u' = D$ . (See Nomenclature for definitions of symbols). Sufficient fundamental relationships are available for calculation of any or all of these properties when the initial state ( $p_i'$  ( $i = 1, 2, \dots N$ ),  $p'$ ,  $\rho'$ ,  $T'$ ,  $n'$ ) and the enthalpy difference ( $h'' - h'$ ) between the initial detonable mixture and the detonation product gas are known. The required relationships can be grouped into several sets of equations: one that



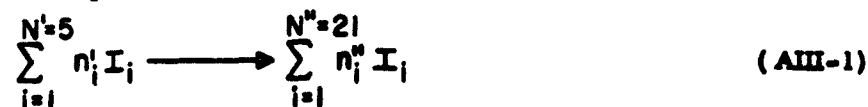
governs the relationships between the state properties such as the temperature, pressure, density and velocity; and the other which determines the chemical composition of the detonation products. The first set consists of the conservation of mass, momentum and energy equations. The second set consists of  $(N'' - A_T = Z_E)$  linearly independent equations for the product gas chemical equilibrium in addition to  $(A_T - 1 = Z_M)$  independent mass balance equations for the conservation of atomic species, Dalton's law of partial pressures, and the equation of state for ideal gases  $(p = \frac{RT}{m})$ . Finally the relationship is required which stipulates that the state of the gases behind the detonation wave satisfies the Chapman-Jouguet condition.

The assumptions involved in these relationships, with the exception of those pertaining to the condensed phase, have been stated previously and will not be repeated here (See Section A of this Appendix, and Appendices I and II). The following additional assumptions pertain to the condensed phase. The only condensed phase present is atomic carbon, assumed to be a pure solid and having a fugacity of unity. The condensed phase occupies a negligible volume and has a partial pressure of zero, even when finely divided and suspended in the product gases. The product gases are insoluble in the condensed phase. These assumptions along with others will be introduced where

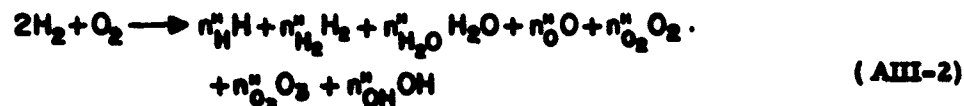
required in the derivation of the basic equations.

### 1. Proposed Scheme of Reaction

To formulate the equilibrium conditions existing at the Chapman-Jouguet point, the chemical species present in the detonation products at the final state must be specified. In the present investigation the initial mixtures were limited to hydrogen and oxygen, either pure or with additives of helium, argon or carbon dioxide. It was found expeditious in the automatic computer program utilized to formulate a general reaction scheme encompassing all additives. The additives and associated detonation products not involved were set equal to zero when computations of the particular mixture were made. Thus for the specific cases encompassed by this investigation, the initial mixture was considered to consist of hydrogen, oxygen, helium, argon and carbon dioxide ( $N' = 5$ ). The final detonation products in thermal and chemical equilibrium are considered to consist of 21 chosen products of reaction ( $N'' = 21$ ) containing carbon, hydrogen, oxygen, helium, and argon, including monatomic carbon in both the gaseous and solid phases; i. e.,  $H$ ,  $H_2$ ,  $H_2O$ ,  $O$ ,  $O_2$ ,  $O_3$ ,  $OH$ ; and  $He$  or  $A$ ; or (when  $CO_2$  is the additive)  $C(g)$ ,  $C(s)$ ,  $C_2$ ,  $C_3$ ,  $CH$ ,  $CH_2$ ,  $CH_3$ ,  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ ,  $CHO$ ,  $CO$ , and  $CO_2$ . The general scheme of reaction encompassing all mixtures considered in this investigation can be represented as follows:



where  $n'$  represents the number of moles of the  $i$ -th component in the initial mixture,  $n''$  represents the number of moles of the  $i$ -th component in the final mixture, and  $I_i$  represents the  $i$ -th chemical component in the initial or final mixture. (The heavier and more complex species (i. e.,  $\text{CH}_3$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{O}_3$ ) were included in the reaction products, even though they were expected to be present normally in negligible amounts at the temperatures and pressures existing in the detonation wave. This was purposely done purely to satisfy the scientific curiosity of this investigator as to the actual magnitudes of these species in the mixtures and under the conditions considered in this investigation.) For the particular case of stoichiometric hydrogen-oxygen mixtures the reaction scheme in Equation (1) becomes



Similar equations can be obtained for stoichiometric hydrogen-oxygen mixtures admixed with helium, argon, or carbon dioxide.

## 2. Equation of State for Ideal Gases

It is assumed that the gaseous components in the initial and final mixtures behave ideally and that the equation of state for ideal gases applies; i. e., idealized values for specific heat and enthalpy (temperature dependent only), fugacity coefficients of unity ( $f_i = p_i$ ), and compressibility factors of unity ( $z = 1$ ).  $\frac{p}{\rho} = \frac{\sum RT}{m} = \frac{RT}{m}$

### 3. Conservation Equations and Rankine-Hugoniot Equations

The conservation equations of mass, momentum and energy, devoid of losses, relating the initial and final states of the detonable mixture, by elimination of the velocity terms from the energy equation and in conjunction with the ideal gas equation of state, can be manipulated to yield the (Rankine-) Hugoniot equation in the following form. (See Appendix II for the presentation of equations and additional details).

$$(h''-h') \frac{m'}{RT} = \frac{1}{2} \left( \frac{P''}{P'} - 1 \right) \left( \frac{\rho'}{\rho''} + 1 \right) \quad (\text{AIII-3})$$

The enthalpy difference  $(h''-h')$  cannot be evaluated directly since the absolute values of enthalpy are not known. However, the absolute enthalpy difference can be expressed in terms of the differences in the heats of formation of the products and reactants by the thermodynamic relationship:

$$\Delta h = (h''-h') = \frac{1}{h'm'} \sum_{i=1}^{N''=21} n_i'' \Delta H_{f(i)} - \frac{1}{n'm'} \sum_{i=1}^{N'=5} n_i' \Delta H_{f(i)} \quad (\text{AIII-4})$$

where  $n'm' = n''m'' =$  mass of either initial or final mixture (conservation of mass).

Expanding the first summation term in Eq. AIII-4 to separate the condensed phase (solid atomic carbon) from the gaseous phase, and replacing the second summation term by its equivalent  $(n' \Delta H_f')$ , and then combining Eqs. AIII-3 and AIII-4 gives:

$$\frac{1}{nRT} \left( n_{C(s)}^n \Delta H_{fC(s)}^n + \sum_{i=1}^{N=21} n_{i(g)}^n \Delta H_{fi(g)}^n - n \Delta H_f^n \right) = 1/2 \left( \frac{p''}{p'} - 1 \right) \left( \frac{p'}{p''} + 1 \right) \quad (\text{AIII-5})$$

Equation AIII-5 can be converted into a form more convenient for numerical evaluation by incorporating the partial pressures ( $p''_i$ ) instead of the mole numbers ( $n_i''$ ) of the product gases. This is

accomplished through the use of the ideal gas equation of state ( $\frac{p}{p'} = \frac{RT}{m}$ ), Dalton's law of additive pressures ( $\sum_{i=1}^{N''=21} p''_i = p''$ ),

and the assumption that the solid carbon occupies a negligible volume ( $V'' = V''_g$ ) and is uniformly dispersed in the gaseous phase. Thus Eq. AIII-5 becomes:

$$\left( \frac{p'}{p''} \right) \left( \frac{1}{p'} \right) \sum_{i=1}^{N=21} p''_i \left( \frac{\Delta H_{fi}}{RT} \right)_{i(g)} - \frac{1}{n} \left[ n' \left( \frac{\Delta H_f}{RT} \right)_{T'} n_{C(s)}^n \left( \frac{\Delta H_f}{RT} \right) \right] = \frac{1}{2} \left( \frac{p''}{p'} - 1 \right) \left( \frac{p'}{p''} + 1 \right) \quad (\text{AIII-6})$$

$$\text{where } \frac{p'}{p''} \text{ is given by } \frac{p'}{p''} = \frac{\frac{n'm' - n_{C(s)}^n m_C}{n'T'}}{\frac{p'T''}{\sum_{i=1}^{N''=21} p''_i m_i}} \quad (\text{AIII-7})$$

#### 4. Conservation of Atomic Species

A mass balance equation stating the conservation of atomic type may be written for each chemical element involved in the proposed reaction scheme (Eq. AIII-1). For atomic species F and G, the law of conservation of mass, taking into account condensed phases in the final mixture yields the following two equations:

$$\sum_{i=1}^{N'} n_i N_{F(i)} - \sum_{i=1}^{N''} n_i^o N_{F(i)} = \frac{n''_G}{p''} \sum_{i=1}^{N''} p''_i N_{F(i)}, \quad (\text{AIII-8})$$

$$\sum_{i=1}^{N'} n_i N_{G(i)} - \sum_{i=1}^{N''} n_i^o N_{G(i)} = \frac{n''_G}{p''} \sum_{i=1}^{N''} p''_i N_{G(i)} \quad (\text{AIII-9})$$

Combining Eqs AIII-8 and AIII-9 and considering solid atomic carbon to be the only condensed phase, yields the following general mass balance equation for any two elements F and G for the specific case defined in the proposed scheme of reaction (Eq. AIII-1):

$$\frac{\sum_{i=1}^{N_F=5} n_i^F N_{F(i)} - n_{C(s)} N_C}{\sum_{i=1}^{N_G=5} n_i^G N_{G(i)} - n_{C(s)} N_C} = \frac{\sum_{i=1}^{N_F=21} p_i^F N_{F(i)}}{\sum_{i=1}^{N_G=21} p_i^G N_{G(i)}} \quad (\text{AIII-10})$$

It is assumed at this point that the other components in the gaseous phase are insoluble in the condensed phase (solid carbon).

The number of chemical elements being considered is  $A_T = 5$  (C, H, O, He, A). Hence, the number of independent atomic mass balance equations obtainable is  $Z_m = A_T - 1 = 4$ . These four equations represent the following ratios of atomic mass conservation:

$$\frac{\text{oxygen}}{\text{hydrogen}} \left( \frac{O}{H} \right); \frac{\text{carbon}}{\text{oxygen}} \left( \frac{C}{O} \right); \frac{\text{helium}}{\text{oxygen}} \left( \frac{He}{O} \right); \text{ and } \frac{\text{argon}}{\text{oxygen}} \left( \frac{A}{O} \right).$$

Taking elements F and G to be oxygen and hydrogen, respectively, Eq. AIII-10 becomes

$$\left[ \frac{2n_{O_2} + 2n_{CO_2}}{2n_{H_2}} \right] \left[ p_{CH}^O + 2p_{CH_2}^O + 3p_{CH_3}^O + 4p_{CH_4}^O + 2p_{C_2H_2}^O + 4p_{C_2H_4}^O + p_{CHO}^O + p_H^O + 2p_{H_2}^O + 2p_{H_2O}^O + p_{OH}^O \right] = p_{CHO}^O + p_{CO}^O + 2p_{CO_2}^O + p_{H_2O}^O + p_O^O + 2p_{O_2}^O + 3p_{O_3}^O + p_{OH}^O \quad (\text{AIII-11})$$

(Conservation  $\frac{O}{H}$ )

Again applying Eq. AIII-10 taking elements F and G to be carbon and oxygen, respectively

$$\left[ \frac{n'_{CO_2} - n''_{C(s)}}{2n'_{O_2} + 2n'_{CO_2}} \right] \left[ p''_{CHO} + p''_{CO} + 2p''_{CO_2} + p''_{H_2O} + p''_O + 2p''_{O_2} + 3p''_{O_3} + p''_{OH} \right] = p''_{C(g)} \\ + 2p''_{C_2} + 3p''_{C_3} + p''_{CH} + p''_{C_2H_2} + p''_{CH_3} + p''_{CH_4} + 2p''_{C_2H_4} + 2p''_{C_3H_4} + p''_{CHO} \\ + p''_{CO} + p''_{CO_2} \quad \left( \text{Conservation of } \frac{C}{O} \right) \quad (\text{AIII-12})$$

Again applying Eq. AIII-10, taking elements F and G to be helium and oxygen, respectively, and assuming the initial mixture to consist only of stoichiometric  $H_2-O_2$  and helium,

$$p''_{He} = \left[ \frac{n'_{He}}{2n'_{O_2}} \right] \left[ p''_{H_2O} + p''_O + 2p''_{O_2} + 3p''_{O_3} + p''_{OH} \right] \\ \left( \text{Conservation of } \frac{He}{O} \right) \quad (\text{AIII-13})$$

Again applying Eq. AIII-10, taking elements F and G to be argon and oxygen, respectively, and assuming the initial mixture to consist only of stoichiometric  $H_2-O_2$  and argon,

$$p''_{Ar} = \left[ \frac{n'_{Ar}}{2n'_{O_2}} \right] \left[ p''_{H_2O} + p''_O + 2p''_{O_2} + 3p''_{O_3} + p''_{OH} \right] \\ \left( \text{Conservation of } \frac{Ar}{O} \right) \quad (\text{AIII-14})$$

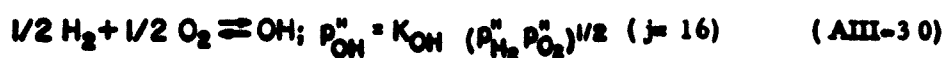
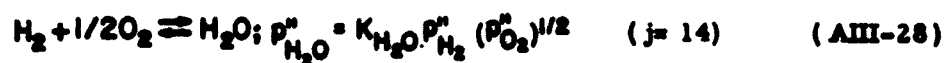
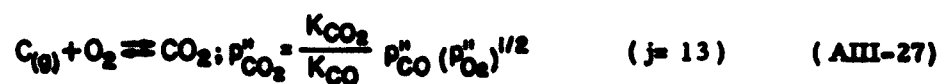
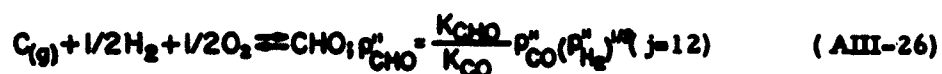
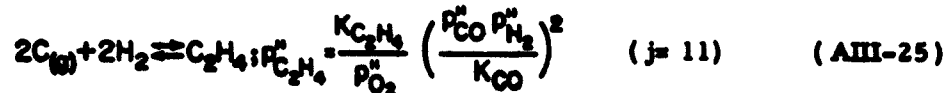
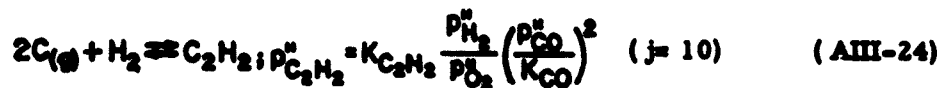
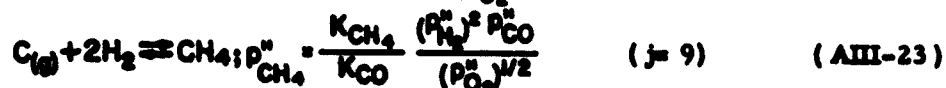
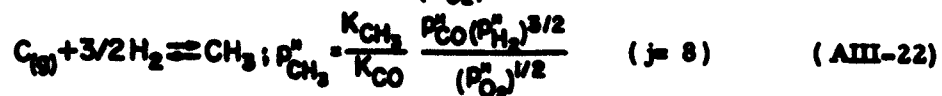
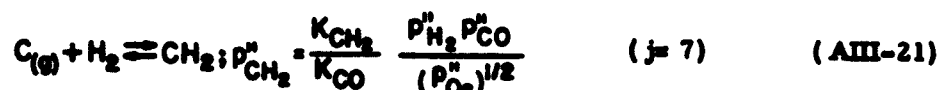
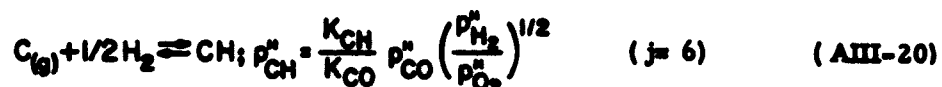
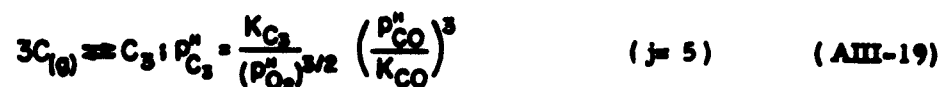
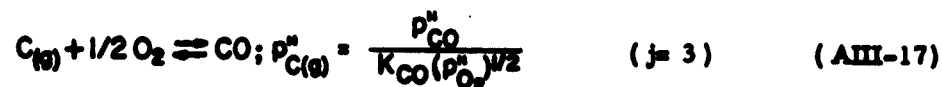
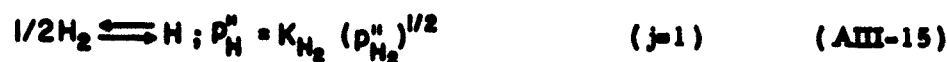
## 5. Chemical Equilibrium Equations.

For the specific C-H-O-He-A system defined in Eq. AIII-1, the

number of chemical elements is  $A_T = 5$ , and the number of chemical components in the final mixture is  $N'' = 21$ . The maximum number of independent chemical equations involving only the gaseous constituents is  $Z_E = N'' - A_T = 16$ . The 16 chemical equilibrium equations involve  $A_R = 3$  chemically reactive atomic species, and  $N'' - A_N = 19$  chemically reactive gaseous components. Since the 16 chemical equilibrium equations involve 19 gaseous components, these equilibrium equations may be used to eliminate 16 of the chemically reactive components of the final mixture, leaving the latter equations expressed in terms of the three remaining chemically reactive components of the final mixture. The three components chosen are  $H_2$ ,  $O_2$ , and  $CO$ . It is expected that these three components will appear in the final mixture in sufficient quantities to permit rapid convergence of the iterative process involved in the calculation procedure used.

Following are the 16 chemical reactions and the corresponding independent chemical equilibrium equations presented as explicit expressions for 16 of the partial pressures ( $p_i''$ 's) of the components in the final mixture, in terms of the chosen three chemically reactive components. (It is assumed that the equilibrium constants are temperature dependent only, i. e.,  $k_i = p_i$ ).





## 6. The Chapman-Jouguet State

The Chapman-Jouguet hypothesis stipulates that in stable detonation wave the detonation products are moving at the local speed of sound relative to the detonation wave front.

$$u' - u'' = D - u'' = a'' \quad (\text{AIII-3 1})$$

$$\text{or } M'' = 1 \quad (\text{AIII-3 2})$$

It can be shown that this is equivalent to the requirement that at the Chapman-Jouguet point, the Rayleigh line, extending from the initial state of the gaseous mixtures ( $\frac{p''}{p'} = 1, \frac{\rho''}{\rho'} = 1$ ), in the region  $\frac{p''}{p'} > 1$ , is tangent to the (Rankine-) Hugoniot curve, i. e., the slope of the Rayleigh line is equal to the slope of the Hugoniot curve at the Chapman-Jouguet point. (See Fig. 1 and Section II-D for details.)

$$\frac{d\left(\frac{p''}{p'}\right)}{d\left(\frac{\rho''}{\rho'}\right)} = \left[ \frac{\frac{p''}{p'} - 1}{\frac{\rho''}{\rho'} - 1} \right] \quad (\text{AIII-3 3})$$

or at the Chapman-Jouguet state,

$$\left[ \frac{\left(\frac{p''}{p'}\right) - 1}{\left(\frac{\rho''}{\rho'}\right) - 1} \right]_{\text{C-J}} \quad \text{is a minimum.} \quad (\text{AIII-3 4})$$

Use of the above Chapman-Jouguet relationships eliminates the necessity for utilization of the isentropic expansion coefficient for the calculation of the detonation velocities and associated parameters.

This eliminates the necessity for stipulating which speed of sound, either "frozen" or "equilibrium", the calculated values are based upon.

For known initial conditions, i. e.,  $p'$ ,  $T'$ ,  $\rho'$ ,  $n_i(p_i')$  and  $n'(p')$ , as well as the thermodynamic data as a known function of temperature, i. e.,  $\Delta H_f(i)$ ,  $\Delta E_g$ ,  $K_j$ , etc., the conservation of mass (Eq. AII-1), the conservation of momentum (Eq. AII-2), Dalton's law of additive pressures, the relationship for the final density (Eq. AIII-7), the (Rankine-) Hugoniot energy equation (Eq. AIII-6), the four conservation of atomic species equations (Eqs. AIII-11 through AIII-14), the sixteen chemical equilibrium equations (Eqs. AIII-15 through AIII-30), and the criteria specifying the Chapman-Jouguet state (Eqs. AIII-31 through AIII-34) constitute a set of 26 non-linear independent equations in 26 unknowns:  $p''$ ,  $T''$ ,  $\rho''$ ,  $u''$ ,  $u' = D$ ,  $p_i''$ , ( $i = 1, 2, \dots, 20$ ) and  $n_{c(s)}$  or  $p''_{c(g)}$ . (If  $n''_{c(s)} = 0$ , then  $p''_{c(g)}$  is an unknown. If  $n''_{c(s)} \neq 0$ , then  $p''_{c(g)} = p_{c(vap)}$ , a known quantity at a specified temperature; and  $n''_{c(s)}$  is an unknown). Simultaneous solution of these non-linear algebraic equations by numerical iterative procedures gives values of the unknown detonation parameters appropriate to the Chapman-Jouguet state.

Such a system of "N" non-linear equations in "N" unknowns in general cannot be solved analytically; i. e., by direct algebraic means. Further, hand solution of these 26 simultaneous non-linear equations would be extremely laborious if not impossible in terms of manhours required. It was found practical and necessary, therefore, in this investigation to make use of a high-speed digital computer (IBM 7090) to solve these complicated equations by numerical iterative procedures. Details of the mathematical method of solution together with the computer program are given in Appendix V of this dissertation.

### C. Additional Chapman-Jouguet Detonation Parameters

Additional detonation parameters and properties of the detonation products can be calculated from the values of the Chapman-Jouguet parameters obtained in the solution of the non-linear equations discussed above. Listed below are the mathematical relationships used to calculate some of the more important detonation parameters.

$$D = u' = \left[ \frac{p'}{p''} \left( \frac{\frac{p''}{p'} - 1}{1 - \frac{p'}{p''}} \right) \right]^{1/2} = \left[ \frac{RT'}{m} \left( \frac{\frac{p''}{p'} - 1}{1 - \frac{p'}{p''}} \right) \right]^{1/2} \quad (\text{AIII-35})$$

$$\frac{p'}{p''} = \frac{(n' m' - n''_{C(s)} m_C) p'' T}{n' T'} \left[ \frac{1}{\sum_{i=1}^{N''=21} p''_i m_i} \right] \quad (\text{AIII-36})$$

$$a_n' = \left( \frac{\gamma_n' RT'}{m'} \right)^{1/2} \quad (\text{AIII-37})$$

$$M' = \frac{D}{a_n'} \quad (\text{AIII-38})$$

$$\gamma_n' = \frac{\left( \frac{C_p}{R} \right)_n'}{\left( \frac{C_p}{R} \right)_{n-1}'} \quad (\text{AIII-39})$$

$$n_g'' = \frac{n' \left( \frac{p'}{p''} \right) \left( \frac{p''}{p'} \right)}{\left( \frac{T''}{T'} \right)} \quad (\text{AIII-40})$$

$$n'' = n_g'' + n_{C(s)}'' \quad (\text{AIII-41})$$

$$\frac{m''}{m'} = \frac{n'}{n''} \quad (\text{AIII-42})$$

$$x_{C(s)}'' = \frac{n_{C(s)}''}{n''} \quad (\text{AIII-43})$$

$$x_{i(g)}'' = \left[ 1 - x_{C(s)}'' \right] \frac{p_i''}{p''} \quad (i = 1, 2, \dots, 21) \quad (\text{AIII-44})$$

$$n_{i(g)}'' = x_{i(g)}'' n'' \quad (i = 1, 2, \dots, 21) \quad (\text{AIII-45})$$

$$n_C'' = n_{C(g)}'' + n_{C(s)}'' \quad (\text{AIII-46})$$

$$\left( \frac{C_p}{R} \right)_{n(g)}'' = \frac{1}{n_g''} \sum_{i=1}^{N''=21} n_{i(g)}'' \left( \frac{C_p}{R} \right)_{n(i)g}'' \quad (\text{AIII-47})$$

$$\left( \frac{C_v}{R} \right)_{n(g)}'' = \left( \frac{C_p}{R} \right)_{n(g)}'' - 1 \quad (\text{AIII-48})$$

$$\gamma_{n(g)}'' = \frac{(C_p/R)_{n(g)}''}{(C_v/R)_{n(g)}''} \quad (\text{AIII-49})$$

$$m_g'' = m'' - x_{C(s)}'' m_C \quad (\text{AIII-50})$$

$$a_{n(g)}'' = \left( \frac{\gamma_{n(g)}'' RT}{m_g''} \right)^{1/2} \quad (\text{AIII-51})$$

$$\gamma_{\text{eff}(g)}'' = \frac{(\gamma_n'' (M')^2 + 1) p'}{p''} - 1 \quad (\text{AIII-52})$$

$$a_{\text{eff}(g)}'' = \left( \frac{\gamma_{\text{eff}(g)}'' RT''}{m_g''} \right)^{1/2} \quad (\text{AIII-53})$$

$$u'' = D = \left[ (p'' - p') \left( \frac{1}{\rho'} - \frac{1}{\rho''} \right) \right]^{1/2} \quad (\text{AIII-54})$$

$$M_{n(g)}'' = \frac{u''}{a_{n(g)}''} \quad (\text{AIII-55})$$

$$M_{\text{eff}(g)}'' = \frac{u''}{a_{\text{eff}(g)}''} \quad (\text{AIII-56})$$

In addition to the above Chapman-Jouguet detonation parameters, it is desirable to be able to calculate the Chapman-Jouguet detonation wave impact pressure. Also of considerable interest are the "equilibrium" specific heats, specific heat ratio, speed of sound and Mach number (compressibility parameter) of the final mixture which include the effects of heats of reaction; i. e., the energy absorbed due to chemical reaction (infinite chemical reaction rates assumed) is allowed to change the chemical composition of the mixture. The so-called "equilibrium" sound speed ( $a''_r(g)$ ) calculated on this basis is different from the so-called "frozen" or normal sound speed ( $a''_n(g)$ ) calculated on the assumption that the energy absorbed does not change the chemical composition of the mixture, i. e., slow chemical reaction rates. The actual sound speed is a value between the "equilibrium" and "frozen" sound speeds since changes in chemical composition will occur at some intermediate finite rate. The relationships pertaining to the impact pressure and to the "equilibrium" conditions are presented in the following paragraphs.

#### D. Chapman-Jouguet Detonation Wave Impact Pressure

When a detonation wave collides with an obstacle in its path a reflected shock wave must be formed in order to maintain conservation of momentum and energy. A further increase in pressure results from this collision. The force of the impact wave as it strikes the

obstacle, i. e., the impact pressure, is composed of the static pressure difference,  $(p''-p')$ , and the force of the flow of the mass of the detonation products behind the wave front,  $\rho''(w)^2$ , where  $w = (D-U'')$ . Thus for a Chapman-Jouguet detonation wave, assuming reflection from a rigid surface normal to the incident wave, (maximum pressure condition), the impact pressure is given by the following relationship:

$$P_T'' = (p''-p') + (D-U'')^2 \rho'' \quad (\text{AIII-57})$$

Substituting for  $(D-U'')$  its equivalent from Eq. AIII-54, Eq. AIII-57 becomes:

$$P_T = (p''-p')\rho''/\rho' \quad (\text{AIII-58})$$

E. Detonation Parameters for Chemically Reacting Gas Mixtures, Including Heats of Reaction.

It is assumed in these derivations that the vapor (carbon gas) and the condensed phase (monatomic solid carbon) in the two-phase detonation products are not in equilibrium and that there is no heat transfer to or from the condensed phase. The condensed phase can then be ignored in the determination of the speed of sound and associated parameters in the products of detonation, and the relationships involving these parameters can be based on the gas phase only.

The analysis and derivation of the mathematic relationships involving the specific heats, the specific heat ratio, the speed of sound



and the Mach number of the final mixture, including the heats of reaction, have been presented by Chu and Edse (52). The general expressions for these quantities in matrix notation are given below:

$$c_{p_{r(g)}}'' = c_{p_{n(g)}}'' + \frac{R''ng}{n'm'} \left[ \frac{\Delta H_j''}{RT} \right] \left[ a_{lj} \right]^{-1} \left\{ \frac{\Delta H_j''}{RT} \right\} \quad (\text{AIII-59})$$

(Row Matrix) (Square Matrix) (Column Matrix)

$$c_{v_{r(g)}}'' = c_{v_{n(g)}}'' + \frac{R''ng}{n'm'} \left[ \frac{\Delta H_j''}{RT} - \Delta \nu_j \right] \left[ b_{lj} \right]^{-1} \left\{ \frac{\Delta H_j''}{RT} - \Delta \nu_j \right\} \quad (\text{AIII-60})$$

$$\gamma_{r(g)}'' = \frac{c_{p_{r(g)}}''}{c_{v_{r(g)}}''} \quad (\text{AIII-61})$$

$$a_{r(g)}'' = \left[ \left( \frac{\gamma_{r(g)}'' RT''}{m_g''} \right) \left( \frac{1 + \left[ \frac{\Delta H_j''}{RT} - \Delta \nu_j \right] \left[ b_{lj} \right]^{-1} \left\{ \Delta \nu_j \right\}}{1 + \left[ \frac{\Delta H_j''}{RT} \right] \left[ a_{lj} \right]^{-1} \left\{ \Delta \nu_j \right\}} \right) \right]^{1/2} \quad (\text{AIII-62})$$

where: "l" or "j" is the general number of a chemical reaction,

$j = 1, 2, \dots, 16; l = 1, 2, \dots, 16.$

$$a_{lj} = \sum_{i=1}^{N''=21} \left( \frac{\nu_{i(l)}}{p_i''/p''} - \Delta \nu_l \right) \nu_{i(j)} \quad (\text{AIII-63})$$

$$b_{lj} = \sum_{i=1}^{N''=21} \frac{\nu_{i(l)}}{p_i''/p''} \nu_{i(j)} \quad (\text{AIII-64})$$

$$\Delta \nu_l = \sum_{i=1}^{N''=21} \nu_{i(l)} \quad (\text{AIII-65})$$

$$\frac{\Delta H_j''}{RT''} = \sum_{j=1}^{N''=21} \nu_{i(j)} \left( \frac{H-E_0}{RT} \right)_i'' + \frac{1}{T''} \left( \frac{\Delta E_0''}{R} \right)_j \quad (\text{AIII-66})$$

#### F. Non-Reacting Normal Shock Wave Parameters

As stated previously, the immediate front of the stable detonation wave is assumed to be a normal shock wave ("von Neumann spike") propagating into the unreacted combustible mixture at the speed of the detonation wave without causing any chemical reactions in the gas (Zone 1, Fig. 29). Further it is assumed that the vibrational degrees of freedom in the gaseous molecules in front and immediately behind the normal shock are completely inactive; i. e., constant specific heats. The analytical analysis involved is essentially the same as that concerned with the propagation of the Chapman-Jouguet detonation wave. The only difference is that for the adiabatic shock front, the net thermal-energy addition to the system is zero (See Fig. 1, Curve AG',  $N=0$ ), while for the detonation wave, the net thermal-energy addition is equal to that converted from chemical energy by combustion (See Fig 1, Curve ADF,  $N=1$ .) Both phenomena can be analyzed as a single-discontinuity system; and the same basic equations of conservation of mass (Eq. AII-1), momentum (Eq. AII-2) and energy (Eq. AII-3) and the (Rankine-) Hugoniot equation (Eq. AII-4) apply to both the normal non-reacting shock wave and the Chapman-Jouguet detonation wave. These basic equations together with the equation of state for ideal gases ( $\frac{p}{\rho} = \frac{RT}{m}$ ),

the assumption of normal ( unreacted) specific heats ( $cp = \gamma_n' R / \gamma_n' - 1$ ), and the expression for Mach number ( $M = u/a$ ) can be manipulated to give the following well-known normal shock wave relationships (4, 205, 209, 226); i. e., properties of the hypothetical "von Neumann spike."

$$\frac{p_{ns}}{p'} = \frac{2\gamma_n'(M')^2 - \gamma_n' + 1}{\gamma_n' + 1} \quad (\text{AIII-67})$$

$$\frac{\rho_{ns}}{\rho'} = \left[ \frac{(\gamma_n' + 1)(M')^2}{(\gamma_n' - 1)(M')^2 + 2} \right] \quad (\text{AIII-68})$$

$$\frac{T_{ns}}{T'} = \frac{p_{ns}/\rho'}{\rho_{ns}/\rho'} \quad (\text{AIII-69})$$

$$M_{NS} = \left[ \frac{(2 + \gamma_n' - 1)(M')^2}{2\gamma_n'(M')^2 - \gamma_n' - 1} \right] \quad (\text{II-70})$$

The normal shock wave ("von Neumann spike") impact pressure can be derived in a manner exactly analagous to that for the detonation wave impact pressure. The relationship is given below:

$$P_{I(NS)} = (p_{NS} - p') \frac{\rho_{NS}}{\rho'} \quad (\text{AIII-71})$$

## APPENDIX IV

### BASIC THERMODYNAMIC DATA

Reliable values, at small temperature intervals, of the thermodynamic properties for the chemical species comprising the initial mixture and the final detonation products were utilized throughout the automatic computation program for the calculation of detonation and shock wave parameters. This was necessary to insure smooth and rapid convergence in the iterative procedures employed. A total of twenty-one selected chemical species containing carbon, hydrogen, oxygen, helium, and argon, including monatomic carbon in both the gaseous and solid phases, were considered to be present in the detonation products under equilibrium conditions; i. e. . H, H<sub>2</sub>, H<sub>2</sub>O, O, O<sub>2</sub>, O<sub>3</sub>, OH, and He or A; or (when CO<sub>2</sub> is the additive) C<sub>(g)</sub>, C<sub>(s)</sub>, C<sub>2</sub>, C<sub>3</sub>, CH, CH<sub>2</sub>, CH<sub>3</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CHO, CO, and CO<sub>2</sub>.

Values of six thermodynamic functions for each of the chemical species considered in the reaction scheme were calculated at 10° K. intervals. The thermodynamic functions for the chemically reactive

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\*It was realized by this investigator that except under unusual circumstances the larger molecules (C<sub>2</sub>H<sub>4</sub>, O<sub>3</sub>, CH<sub>3</sub>, CH<sub>4</sub>, C<sub>2</sub>, H<sub>2</sub>) considered to be present in the reaction products would be present in very small amounts under the temperatures and pressures existing in the detonation wave. However, since the automatic computation program could easily accomodate these species, it was decided to determine quantitatively the actual magnitudes of these constituents as a function of initial pressure and mixture composition---if only to satisfy scientific curiosity.

gaseous species were the following:  $(C_p^0/R)$ , dimensionless molal heat capacity at constant pressure;  $(F^0-E_0^0)/RT$ , free energy function;  $(\frac{H^0-E_0^0}{RT})$  enthalpy function;  $\Delta H_f/R$ , dimensionless heat of formation;  $S^0/R$ , entropy function; and  $\ln_e K_p$ , natural logarithm of the equilibrium constant in terms of partial pressures. For the chemically non-reactive species (He and A), the same thermodynamic properties were considered. However, the equilibrium constant was eliminated; and  $C_p^0/R$  and  $(\frac{H^0-E_0^0}{RT})$  were assigned constant values since for inerts these functions do not change with temperature (Note that  $(\frac{H^0-E_0^0}{RT}) = \frac{\Delta H_f}{RT}$  for inerts since  $\Delta E_0^0 \approx 0$ ). For solid carbon (C(s)),  $\ln_e K_p$  was replaced by the natural logarithm of the vapor pressure of monatomic carbon; i. e.,  $\ln_e p_C(\text{vap})$ .

The basic thermodynamic data from which the computations were made were: the heat of reaction for the formation of the specie from the elements in their standard states of aggregation at  $0^\circ\text{K}$  ( $\Delta E_0^0$ ), heat capacity, free energy and enthalpy. These data were gathered from the most recent and reliable sources available. All the data (7, 13, 54, 130, 131, 144, 152, 228, 271, 277, 286) were found at  $100^\circ\text{K}$  intervals. All the basic data were converted to non-dimensional form. The entropy and equilibrium constants were computed from the modified basic data at  $100^\circ\text{K}$  intervals for all species.

The entropy data were calculated from enthalpy, free energy and  $\Delta E_0^0$  from the following fundamental relationship:

$$\left(\frac{S^\circ}{R}\right)_i = \left(\frac{H^\circ - E_0^\circ}{RT} + \frac{\Delta E_0^\circ}{RT}\right)_i - \left(\frac{F^\circ - E_0^\circ}{RT} + \frac{\Delta E_0^\circ}{RT}\right)_i \quad (\text{A-IV-1})$$

The equilibrium constant data were calculated from free energy and  $\Delta E_0^\circ$  data by the following basic expression:

$$\ln_e K_p = - \sum_i \nu_i \left( \frac{F^\circ - E_0^\circ}{RT} + \frac{\Delta E_0^\circ}{RT} \right) \quad (\text{A-IV-2})$$

where  $\nu_i$  is the stoichiometric mole number of the  $i$ -th component in the chemical reaction, positive for the products and negative for the reactants. The chemical reaction in this case is the reaction of formation of one mole of the specie from the elements in their standard states of aggregation.

The vapor pressure of monatomic carbon was calculated from free energy and  $\Delta E_0^\circ$  data for solid and gaseous carbon by the following relationship:

$$\ln_e p_{C(\text{vap})} = - \left( \frac{F^\circ - E_0^\circ}{RT} + \frac{\Delta E_0^\circ}{RT} \right)_{C(g)} + \left( \frac{F^\circ - E_0^\circ}{RT} + \frac{\Delta E_0^\circ}{RT} \right)_{C(s)} \quad (\text{A-IV-3})$$

The dimensionless heats of formation of the specie from the elements in their standard states of aggregation at 0°K were obtained from enthalpy and  $\Delta E_0^\circ$  data by the following expression:

$$\left(\frac{\Delta H_f}{RT}\right)_i = \left(\frac{H^\circ - E_0^\circ}{RT}\right)_i + \left(\frac{\Delta E_0^\circ}{RT}\right)_i \quad (\text{A-IV-4})$$

( Refer to the Table of Nomenclature for detailed definitions of the thermodynamic functions. )

All the 100°K. data were examined and treated where necessary to insure consistency throughout. First, second, third and fourth order differences were computed on the Univac 1103 A digital computer for each of the thermodynamic functions at every 100°K interval over the entire temperature range. All differences were examined in order to locate all points of inconsistency in the data. All regions of inconsistency were eliminated by the use of graphical smoothening techniques. Smooth curves were drawn through each region of inconsistency and new values were read from the smoothened curve for those points which appeared to be out of line. Highly consistent values at 10°K. intervals for each of the thermodynamic functions over the entire temperature range were obtained from the 100°K interval data by the Aitkens fourth-order interpolation method. The temperature range covered for the majority of the chemical species considered was 100°K. to 6000°K. Exceptions were  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OH}$ , the temperature range covered being 100°K to 1000°K. for the former and 300°K to 1500°K for the latter. Accuracy of the data calculated is felt to be at least as good as that of the data obtained from the original sources.

All the thermodynamic data in  $10^{\circ}\text{K}$  intervals were compiled and presented in tabular form. Because of the bulk of these tables of thermodynamic data, it was decided not to include them as an integral part of this dissertation. The data were instead incorporated as the main body of a technical report. This report has been published and is available as an Air Force Technical Report (318).



## APPENDIX V

### CALCULATION OF DETONATION PARAMETERS

The program used in this investigation for the calculation of detonation and shock parameters was written in Fortran language, and all computations were performed on an IBM 7090 electronic digital computer. The overall computation program was divided into two main parts. The first part consisted of the product composition calculation together with determination of the final temperature, pressure and density at the Chapman-Jouguet point. The second part consisted of the calculation of additional steady-state Chapman-Jouguet detonation parameters based on these values, the calculation of parameters including the heats of reaction ( $C_{p,r(g)}''$ ,  $C_{v,r(g)}''$ ,  $\gamma_{r(g)}''$ ,  $\sigma_{r(g)}''$  and  $M_{r(g)}''$ ), and the calculation of the non-reacting shock parameters ("von Neumann spike"). A flow diagram for the calculation of detonation product composition is given in Fig. 30.

The calculation of the detonation parameters was accomplished by the simultaneous solution by numerical iterative procedures of the group of nonlinear equations presented in Appendix III. Determination of the product composition, temperature, pressure and density at the Chapman-Jouguet point was accomplished by means of a triple-contained iteration procedure. More specifically the calculations involved a composition iteration to determine the partial pressures satisfying the atomic mass balance relationships; inside a Hugoniot

iteration to satisfy both the atomic mass balance and Hugoniot relationships and thus establish a point on the equilibrium Hugoniot; inside of a Chapman-Jouguet iteration to determine the final detonation product composition, temperature, pressure and density which satisfied the atomic mass balance equations, the Hugoniot and the Chapman-Jouguet relationships.

The product composition calculation comprised the major portion of the problem. The composition iteration was based on initial estimates of the detonation temperature and of the composition of the chosen major chemically-active constituents in the detonation products,  $H_2$ ,  $O_2$ , and  $CO$ . (For the mixtures without  $CO_2$  in the initial mixture,  $CO$  was omitted.) The calculated values of final temperature and composition at the Chapman-Jouguet point for a particular initial condition (initial mixture composition and initial pressure) were used to calculate new estimates of final temperature and composition for the same mixture at an increased initial pressure.

The actual calculation of detonation parameters on the IBM 7090 computer proceeded according to the following steps (See Fig. 30). The thermodynamic data for all species involved in the reaction products (See Eq. III-1 Appendix III, and Appendix IV.) were stored in the computer as temperature dependent data, along with the program.

The initial conditions ( $p'$ ,  $T'$ ,  $n'_i$ ) were obtained from input cards for each initial condition. The initial estimates of  $T''$ ,  $p''_{H_2}$ ,  $p'_{O_2}$  and  $p''_{CO}$  were obtained from input cards of calculated from values based on previous runs contained within the storage capacity of the machine.

The values of  $T''$  and  $p''_{H_2}$  were then fixed, and the iteration on  $p''_{O_2}$  and  $p''_{CO}$  was performed until convergence on both was reached within a specified tolerance (when the difference between two successively calculated values of  $p''_{O_2}$  and  $p''_{CO}$  was less than  $10^{-5} \times p''_i$ ,  $i = CO, O_2$ ). This condition satisfied the mass balance equations for the particular chosen  $T''$  and  $p''_{H_2}$ . Involved in this iteration were the calculations by means of the equilibrium relationships, of all the  $p''_i$ 's based on the then current values of  $T''$ ,  $p''_{H_2}$ ,  $p''_{O_2}$  and  $p''_{CO}$ . In the calculations it was initially assumed that solid carbon ( $C_{(s)}$ ) was not present. When it was detected within the calculation procedure according to specified tests ( $p_{c(g)} > p_{c(vap)}$ ), it was entered into the calculations as  $n''_{c(s)}$ ; and  $p''_{c(g)}$  was set equal to  $p_{c(vap)}$ . Otherwise, it was assumed that no solid carbon was present; and all parameters involving  $C_{(s)}$  were set equal to zero.

Iteration was next performed on the final temperature ( $T''$ ) until the Chapman-Jouguet condition for detonation was satisfied. Again

for each temperature used in this iteration, the iterations on the  $p''_{H_2}$  had to be satisfied. In the temperature iteration, to arrive at the Chapman-Jouguet point, at each chosen final temperature values were calculated for points on the Hugoniot equilibrium curve ( $p''/p'$  and  $\rho'/\rho''$ ), for temperatures of  $(T'' + 3^\circ K)$  and  $(T'' - 3^\circ K)$  in order to obtain an accurate estimation of the slope of the Hugoniot curve at the  $T''$  value. When the  $T''$  iteration converged to within specified tolerances, ( $10^{-4}$  x slope of the Hugoniot at that point) the iteration procedure was considered to have converged completely at the Chapman-Jouguet point with all three conditions being met; i. e., the Chapman-Jouguet point was reached when the atomic mass balance equations, the Hugoniot energy equation and the Chapman-Jouguet relationships was satisfied.

The results from the first portion of the calculation, i. e., Chapman-Jouguet detonation product composition, temperature and density, were used as the input for the calculation of the remaining Chapman-Jouguet detonation parameters, the parameters including the heats of reaction, and the non-reacting shock parameters. These parameters were calculated according to the relationships given in Appendix III, Eqs. AIII-35 through AIII-71. The calculations for the detonation parameters which included the heats of reaction were relatively straight forward, once the product gas composition was known. Involved was the multiplication of three matrices: a row

matrix, an inverted square matrix and a column matrix. (See Eqs. AIII-59 through AIII-66, Appendix III.) These matrices were solved on the IBM 7090 digital computer using available matrix sub-routines.

The detonation and shock parameters obtained as a result of the calculations were printed out in tabular form. The tabulated results are presented in Section IV and Appendix VIII of this report. The mixtures involving carbon dioxide required more machine time than mixtures involving argon or helium as the additive or pure stoichiometric hydrogen-oxygen. Approximately 2-1/2 minutes of machine time was required for the initial read-in of the thermodynamic data. In addition, for the hydrogen-oxygen-carbon dioxide mixtures, about 12 seconds were required for determination of the final product composition, the final temperature, pressure and density at the Chapman-Jouguet point, for a particular initial condition. Approximately 8 seconds were required for the hydrogen-oxygen-argon (or helium) and the pure stoichiometric hydrogen-oxygen mixtures per initial condition. To complete the calculation of the remaining detonation parameters, the parameters including heats of reaction, and the non-reacting shock parameters required approximately 8 additional seconds per case.

APPENDIX VI  
EXPERIMENTAL EQUIPMENT, INSTRUMENTATION  
AND TECHNIQUES

A. General

As indicated in Section III, the principal components of the high-pressure detonation installation consisted of a detonation tube, a gas handling system, an ignition system, a velocity measuring system, and a pressure measuring system. Because of the danger to personnel due to possible inadvertent explosions during some of the experiments, the detonation tube and a portion of the gas handling system were physically isolated in a combustion test cell constructed of two-foot thick reinforced concrete walls and provided with explosion-proof fans, blow-out door panels and roof, and observation sections. Fig. 2 is an overall photograph of the high-pressure detonation test installation located in the test cell. All operating controls were located in the control room area which was separated from the test cell by the concrete protecting wall. All operations were remotely controlled from the control room. Extension shafts were led through holes in the dividing wall to permit remote operation from the control room of critical valves located in the test cell to seal off the detonation tube and vent the explosive gases. The inlet portion of the detonation tube and the combustible gas gage panel located in the test area were viewed through a 2' x 3' visual observation section consisting of three pieces of 1" thick bullet-proof plate glass each separated by an air gap of approximately 8". The exit end of the

detonation tube was observed by means of closed circuit television.

High pressure gas cylinders containing the test gases were installed in a test rack located outside the building. Three separate manifolds were mounted on the rack and were used for hydrogen, oxygen and additive (He, A or CO<sub>2</sub>), respectively. High-pressure copper tubing in continuous lengths was connected to each manifold and led through holes in the building walls and floors to a valve system located in the test cell. From the valve system, the tubing was run through holes in the concrete dividing wall to the main control and instrumentation console located in the control room. Also incorporated in the installation were a high pressure dry air system and a vacuum system. Fig. 3 is a photograph of the main control and instrumentation console.

High-pressure heavy-walled 1/4" (.062"-wall) copper tubing was used for all compressed gas lines except portions of the high-pressure air supply which were 1/4" (.042"-wall) stainless steel tubing. All tubing joints and connections were accomplished by silver solder brazing whenever possible to eliminate possibilities of leakage. Grove\* high-pressure (3000 and 6000 psi) stainless steel fittings were used throughout the installation.

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\*Grove Valve and Regulator Co., Oakland, California

Gas leaks were detected by means of a Johnson-Williams\* combustible gas sensor which automatically started two large exhaust fans located in the test cell if an explosive mixture was indicated there. Also remotely operated shut-off ( solenoid) valves were installed in the oxidizer and fuel lines to permit rapid and positive shut-off of these gases at the gas source in the event of emergency.

Various ranges of Duragage\*\* bourdon tube pressure gages ( 0-15, 0-160, 0-800, 0-1000, 0-2000 psi) were used to measure compressed gas pressures and pressure in the detonation tube prior to ignition, i. e., initial pressure. For measurement of low initial pressures, vacuum-and pressure-mercury manometers were used. The bourdon tube pressure gages were calibrated with precision Heise\*\*\* gages, which have a guaranteed accuracy of 0.2 of 1% of the full gage scale range.

The compressed gases used were oxygen, hydrogen, helium, argon and carbon dioxide. They were taken directly from the standard compressed gas cylinders furnished by the commercial suppliers and were used without further purification. The oxygen

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\*Johnson-Williams Co-Palo Alto, California

\*\* Manning, Maxwell and Moore, Inc. - Stratford, Conn.

\*\*\* Heise Gage Co. - Newton, Conn.



(General Dynamics) was stated by the manufacturer to contain 99.5%  $O_2$ , 0.4A, and 0.1 $N_2$ ; the hydrogen (Burdette) to contain 99.9%  $H_2$  and 0.1%  $O_2$ ; the helium (Bureau of Mines) to contain 99.9% He and 0.1%  $N_2$ ; the argon (National Gas Cylinder) to contain 99.9% Ar and 0.1%  $N_2$ ; and the carbon dioxide to contain 99.9%  $CO_2$ .

#### B. Detonation Tube

The detonation tube was designed on the assumption that the maximum initial pressure of any detonable mixtures to be investigated would be limited to 100 atmospheres. With this initial pressure, assuming a pressure rise of 20 to 1 at the Chapman-Jouguet point for the most energetic system to be investigated, (i. e., pure hydrogen-oxygen) and a multiplication of 1.5 due to the reflected wave, the maximum pressure in the tube could be expected to reach approximately 45,000 psi. On the basis of these calculations, the detonation tube was fabricated from a single 16-foot length of "Double Extra Heavy" type 304 stainless steel seamless tubing with an outside diameter of 2-1/2 inches and a wall thickness of 1/2 inch. Stainless steel was selected for its corrosion resistance as well as for its strength characteristics. The calculated bursting pressure of this tube was 60,000 psi, which was probably a conservative estimate. It was considered that the any pressure in excess of the Chapman-Jouguet pressure, such as that predicted for the von-Neumann "spike," would be of such short duration that the inertia of mass of metal

surrounding the tube bore would be sufficient to contain it. However, as mentioned previously, the detonation tube was located in the combustion test cell in the event the above-mentioned assumptions were not altogether valid. As it so happened, the maximum initial pressure for any detonable mixture investigated was 50 atmospheres; and no difficulty with the detonation tube itself was experienced.

The detonation tube bore was precision machined and reamed to 1.5-inches inside diameter within close tolerances of concentricity and uniformity. After machining, the inside wall was lapped until a smooth surface was obtained. A heavy tapped sleeve, designed to accommodate the "O" ring sealed igniter assembly, was welded to the inlet end. A heavy flange was welded to the exit end of the detonation tube. Pressure and vacuum tight closures at both the inlet and outlet ends of the detonation tube were obtained through the use of rubber "O" ring seals. The "O" ring grooves were incorporated in the inlet end capped sleeve and the exit end cover plate, respectively. Five holes, spaced at 2-foot intervals apart, were drilled into the detonation tube. Threaded bosses were welded to the tube at these stations to accommodate flush-mounted ionization probes. The first probe station was located 7 feet from the igniter. This distance is greater than the distance indicated by Laffette (193) Greene (136) Bollinger and Edse (22, 25, 26) and others as required to attain

stable detonation in the mixtures investigated. Great care was taken in locating properly the ionization probe bosses in the detonation tube. As a result, the station-to-station distances were determinable to within several thousands of an inch. An additional hole, located at 13-3/4 feet from the igniter end of the tube, was tapped in the tube wall to accomodate a flush-mounted pressure transducer. Fig. 4 is a drawing of the detonation tube, including the locations of the ionization probes and pressure transducer.

The detonation tube was submerged in a temperature-controlled water bath (See Fig. 5) in order to provide a constant initial temperature of the gas mixture. A water pump was used to circulate the water in the tank in order to minimize temperature gradients along the detonation tube. Three two-kilowatt electric heaters mounted in the bottom of the water tank were used to heat the water to the desired temperature reference level. A Fenwal\* thermostatic type of controller was used to supply power intermittently to the heaters to maintain the constant temperature base. The temperature was controlled to within  $\pm 2^{\circ}$  F. at  $80^{\circ}$  F., which was more than adequate for the tests. After the detonation system became operative it was found necessary to enclose the inlet and outlet detonation tube gas lines and fittings in sections of 1-1/2" O.D. copper tubing and water cool them during a detonation test run. This was done to prevent destruction of the 1/4" copper lines and fittings due to

\*Fenwal Incorporated, Ashland, Mass.

exposure to the high-temperature and high-pressure detonation products. Water cooling of these lines was found to be particularly beneficial at the higher initial detonation pressure where almost invariably without water-cooling, destruction of the inlet and/or outlet tubes would be experienced. Fig. 5 is a photograph of the detonation tube installation in the test cell, together with the ionization probes, pressure transducer and pressure measuring equipment.

### C. Gas Handling System

Fig. 6 is a flow diagram of the high pressure detonation system used in these tests. Three independent and complete flow measurement and control systems were used, for the hydrogen, oxygen and additive (He, A, CO<sub>2</sub>), respectively. Provisions were incorporated for accurate "mixing-on-flow" of these gases in any desired proportion to permit immediate testing. This procedure avoided the difficulties and dangers involved in filling and storing large amounts of uniformly premixed gases for a series of experiments. All three flow systems were essentially identical. Taking the oxygen system as an example, the compressed gas was taken from standard gas cylinders and passed through high-pressure manifold filters filled with fiberglass to remove any metal chips and turnings present in the gas cylinders prior to entering the oxygen manifold. It was found that these particles would damage solenoid valves and pressure

regulators, clog up gas lines, and impair operation of needle valves if not removed. From the manifold the oxygen was passed through a silica gel trap to remove any oil and/or water vapor and then through a silica gel dust filter. The gas was then passed through a Grove "mity mite" Model 94W pressure-reducing regulator before being led into a specially designed high pressure "plugged" or "packed" flow meter to measure the small volume flow rates. Preliminary investigations were made with various designs of flow meters packed with different types of material; e. g. , cotton, glass, wool, glass beads, sand, or wire screen. The results obtained indicated that a flow meter firmly packed with layers of wire screen was the most satisfactory arrangement from the viewpoint of pressure drop, calibration stability, maintenance and operation. On the basis of these investigations the final design flow meter used was packed with layers of very fine mesh ( 10,000 mesh) brass screen held in place by spring compression. The final packed flow meter details are shown in Fig. 7 and Fig. 8 as an exploded view of the meter. Sufficient layers of screen were added so that the pressure drop across the meter was sufficient to be measured easily for the desired flow rate with a differential-pressure gage. Various ranges of flow rates for a fixed pressure drop could be obtained by varying the amount and/or mesh wire screen in the flowmeter. The pressure drop across the flow meter was measured by a Barton\* Model 200 differential-

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\*Barton Instrument Corp. - Los Angeles, California

pressure indicator having a range from 0 to 20 inches of water for line pressures up to 2500 psig. For a fixed upstream pressure on the flow meter, the pressure drop was calibrated as a function of the flow rate by means of a vacuum displacement flow calibrator which was integrated into the gas flow system. The calibrator automatically measures the time required to pressurize a known volume from a near vacuum to 1 atmosphere with a constant flow of gas from a flow meter. The gas volume is obtained by dividing the calibration volume by the pressurization time and applying corrections from PVT data.

Downstream of the flow meter, two needle valves in series were used to provide fine control of the mass flow rate of oxygen. The gas was throttled by a Grove "mity-mite" back pressure regulator to eliminate fluctuations in the flow caused by flow rate changes of the hydrogen and/or additive. Grove Model 15 H small volume flow loaders were used to regulate the air pressure to domes of the reducing and back pressure regulators. To provide minor adjustment of the dome pressure to the reducing and back-pressure regulators, fine control needle valves were used to change the pressure of the trapped gas. Fig. 9 is a photograph of the flow control equipment rack located in the test cell which was used in the "mixing-on-flow" system.

All gases were transferred through separate lines to a heavy-walled stainless steel mixing chamber (4-inch OD, 1-inch ID,

14"-inch long) mounted in the flow equipment rack located in the test cell. Direct impingement of the gases, together with turbulence produced by stainless steel filings in the chamber cavity, provided excellent uniform mixing of the flowing gases. From the mixing chamber the premixed gases were transferred to the detonation tube. Appropriate valving was incorporated in the system so that the detonation tube could be purged with dry air prior to being filled with the explosive mixture of gases. When initial pressures higher than atmospheric were desired, the detonation tube was vented to the atmosphere through a needle valve adjusted to maintain the desired back-pressure in the detonation tube exit. (In initial tests, a back-pressure regulator was used instead of the needle valve in the detonation tube exit line. The regulator proved to be unsatisfactory because it required continued maintenance and inspection to insure proper operation.) Remotely operated valves were used to seal off the detonation tube and to vent the premixed gases in the mixing chamber and gage manifold lines in order to prevent explosion in this portion of the system.

A high-pressure exploding wire igniter was used to ignite the gas mixtures. Design details and an exploded view of the igniter are shown in Figs. 10 and 11. Positive ignition was accomplished by melting a 0.0019-inch nichrome bridge wire, incorporated as

part of a standard Dupont No. 1 bridge-plug, \* (See Fig. 11) with current from a 5000 volt power source. The igniter body was provided with a threaded end section to permit assembly into the detonation tube inlet. Sealing was accomplished by means of an "O" ring located in the igniter body shoulder.

#### D. Velocity Measuring System

##### 1. General

The detonation wave velocity was determined by means of the ionization probe technique. The velocity measuring system consisted primarily of five flush-mounted ionization probes positioned in a plane perpendicular to the tube axis and located at 2-foot intervals along the detonation tube (See Figs. 4 and 5,) to detect the passage of the detonation wave; a 4-channel 10-megacycle electronic chronograph to measure the time required for the detonation wave to travel between a set of probe stations; and a 500 volt variable direct current probe power supply. A simplified block diagram of the detonation velocity measuring system, as well as the pressure measuring system, is shown in Fig. 12.

##### 2. Ionization Probes

The ionization probes were designed for high-pressure as well as for sub-atmospheric application. Several different types of probes

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\*E.I. Dupont de Nemours Co., Inc., Explosive Dept - Wilmington, Del.



were tested, including two-electrode and single-electrode configurations. Also several different insulating materials used to isolate the electrode (s) were tested, including glass, phenolic, nylon, acrylate plastic and Teflon (polytetrafluorethylene). Only one design gave satisfactory overall performance: the single central electrode covered with a cylindrical sheath of Teflon as the insulator, with the metal wall serving as the second electrode. Use of the single central-insulated electrode configuration permitted the use of larger electrode gaps. This minimized difficulties encountered through shorting of the probes by condensed moisture and carbon deposits. Teflon was found to be superior to the other insulators for this investigation because of its greater thermal stability and chemical stability. Also because when clean, it has less tendency to form conducting paths as a result of moisture deposit, thus minimizing sporadic triggering of the counters. Very little difficulty was experienced with this probe in detonation tests run at initial pressures under 10 atmospheres. However, at higher initial pressures, the Teflon had a tendency to vaporize, requiring more frequent checking and replacement of this portion of the probe assembly. The final ionization probe details are shown in Fig. 13. A photograph of the assembled and disassembled probe is presented in Fig. 14. The Teflon rod was drilled slightly undersized; and a No. 2-56 stainless steel screw, used as the electrode, was threaded into it. The probes were provided with stainless steel 1/4 inch

tube male fittings to permit them to be screwed into the bosses located on detonation tube. Fig. 15 shows the probe mounted in the detonation tube. A rubber "O" ring located in each fitting shoulder was used to pressure-seal the probes in the detonation tube boss. The ionization probe assembly was designed so that the ends of the Teflon insulator and the electrode were flush with the inner wall of the tube. Bridgeman (36) "unsupported area" packing was used to pressure seal the Teflon insulator in the probe housing. The ionization probe assembly was designed so that the ends of the Teflon insulator and the electrode were flush with the inner wall of the tube when the assembly was tightened fully. The probes were connected by identical lengths of low capacitance shielded coaxial cable to a junction box which provided connections to the counters and to a 500 volt variable direct current power supply. The cables were isolated from the high voltage igniter cable to prevent spurious starting of the counters by pickup of ignition impulse.

### 3. Chronograph System

The electronic chronograph system used in this investigation consisted of four Hewlett-Packard FR 38A/U Frequency Meters or Time Internal Counters and associated electronics. Each frequency meter consists of a 100-kilocycle crystal-controlled oscillator, a pulse-forming circuit, an electronic gate and a series of MX-1636/U Time

Interval Units which enables the instrument to measure time intervals from 0.1 microsecond to 10,000,000 seconds in discrete intervals of 0.1 microsecond.

The Time Interval Counter essentially provides a direct reading of elapsed time between any two events where the events can be translated into changing voltages. Timing is started and stopped by independent voltages. The electronic gate is opened when the first event (or voltage) occurs, admitting the time base pulses to the 10 megacycle time interval unit. Each pulse from the 100 kilocycle oscillator is multiplied by 100 in each of the counters and is counted by the decade units as a continuous series of 0.1 microseconds increments of time. Occurrence of the second event (or voltage) closes the electronic gate, which stops the pulses from the oscillator and completes the count. The elapsed time between the first and second event is indicated on the Time Interval Units as a whole number of microseconds increments plus tenths of a microsecond indicated on the tenths-microsecond gauge.

A schematic wiring diagram of the electronic chronograph pulse triggering circuit is shown in Fig. 16. The stop and start mechanisms for generating the triggering pulses to the counters were provided by the five ionization probes. Prior to ignition of the detonable mixture, a 450 volt direct current potential (B-supply) in series with

a 33 Kohm load resistor was impressed across the probe housing (ground) and the electrode, charging the .001 Mfd. capacitors connected to the probes. Following initiation of detonation, when the detonation wave passed the probes, the resulting ionization of the hot products gases increased the gas conductivity across the gaps sufficient to complete the electrical circuit thereby allowing the 0.001 Mfd. capacitors to discharge. These discharges caused very sharp positive voltage pulses to develop across the 33,000 ohm resistors. These pulses were used to trigger the start and stop inputs of the four 10 megacycle Time Interval Units. In the system used in this investigation, the pulse from the Number 1 probe was used to trigger the start inputs of all four counters as the detonation wave started down the tube. As the detonation wave passed the succeeding four probes, the signal from each probe triggered the stop and input for each succeeding counter. Thus four time measurements of successively longer distances of travel by the wave front were obtained during any single run. The average detonation velocity between probe stations was obtained by dividing the probe spacing by the time required for the wave to pass between the probes.

In preliminary check-out tests of the four-channel chronograph system, it was found that use of four independent crystal oscillators

instead of one complicated the channel-synchronization problem, since it was found that divergence of frequency and phase existed. Therefore, a single 10 kilocycle crystal-controlled oscillator with a temperature regulated crystal oven maintained at 65° C. was used to control the timing signal and provide the standard frequency counted by the Time Interval Units of all the counters. This "standard" 100 kilocycle oscillator was calibrated by "beating" its output against the 10 megacycle signal broadcast by the National Bureau of Standards radio station WWV, the crystal being adjusted until zero "beat" was obtained.

In addition to the pulse-producing circuitry, provisions were incorporated to simulate the "start" and "stop" signals from the ionization probes. This facilitated the testing of each counter unit prior to actual velocity measurements and helped in detecting spurious effects arising from misadjusted multivibrators, frequency dividers, or oscillator frequencies as well as defective ionization probes and probe leads. Simulated "start" signals were generated by depressing a momentary switch which effectively short-circuited all the probe gaps through 10 kilo ohm resistors, discharging the 001 fd. condensers and simultaneously producing "start" pulses for all the counters (common start). Common "stop" pulses to stop all counters simultaneously were generated by a similar process.

Provisions were also incorporated for generation of simulated individual "stop" signals for any counter. Means were also incorporated for checking out the entire chronograph system prior to the actual detonation firing through the use of a bank of five ionization probes mounted in a rack external to the detonation tube, each probe being connected to the coaxial cable leading to the appropriate counter and all probe bodies being grounded to a common ground. All counters were started by shorting out the first probe, and any other counter was stopped by shorting out the following appropriate probe. By this means all electrical leads and connectors as well as the counters making up the entire chronograph system were checked out prior to the actual test run.

#### **E. Pressure Measuring System**

##### **1. General**

Measurements of detonation pressure reported thus far in the literature in general have not been too satisfactory. (Refer to Literature Review, Section IIH-2 of this dissertation for details.) For the most part the measuring systems utilized have suffered from insufficient rise time characteristics which prevented faithful reproduction of a shock-type driving function. Also the true wave form of the driving function, i. e., pressure-time history, was obscured by the "ringing" of the pressure pick-up at its damped natural frequency; and the observed response was not in phase with the true

phenomena. As a result of these effects, a phenomenon having a complex wave form appeared in the transducer's output in a distorted and often misleading form, making it difficult if not impossible to make an accurate interpretation of the true driving force, i. e., pressure.

In the present investigation, in order to minimize these defects, a fast response pressure measuring system incorporating a high-speed on-line electronic compensator was used. The compensator automatically and continuously corrected for the dynamic errors due to the effects of mass and friction of the moving elements in the pressure pickup during transient measurements, yielding a true picture of the driving function, i. e., pressure. It accomplishes this under optimum conditions at response times on the order of a microsecond, or several times the resonant frequency of the transducer itself.

The pressure measuring system consisted of a Kistler\* SLM Model 605 miniature piezoelectric quartz crystal pressure transducer, a Kistler model 656 dual-channel amplifier-calibrator, an electronic compensator-Dresser Dynamics\*\* Model DATTA (Dynamic Analog Transistorized Transducer Analyzer), a Tektronix\*\*\*

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\* Kistler Instrument Corp., 15 Webster St., North Tonawanda, N. Y.

\*\* Dresser Dynamics, Div. Dresser Industries, Northridge, Calif.

\*\*\* DuMont Laboratories, Inc., Clifton, N. J.

Model 535 oscilloscope using a Tektronix type 53C preamplifier plug-in unit, and a DuMont Model 302 oscilloscope camera with a Polaroid Land camera back. A block diagram of the pressure measuring system, integrated with the velocity measuring system is shown in Fig. 12. A photograph showing the physical arrangement of the pressure measuring instrumentation in the test cell is shown in Fig. 2. Under actual operating conditions the output signal voltage from the transducer was coupled to the electrometer follower circuit of the amplifier-calibrator through special low-noise, high-resistance cable. The output from the electrometer follower went to the "DATTA" electronic compensator, and the compensated output from the "DATTA" was taken to the oscilloscope. The oscilloscope deflection produced by the transducer was then photographically recorded with the oscilloscope camera. The components of the pressure measuring system are discussed in the following paragraphs.

## 2. Pressure Transducer

A pressure transducer suitable for use in these tests had to have the following general characteristics: be mechanically capable of withstanding erosion due to the products of detonation, be insensitive to temperature transients during the pressure measuring period, have practically no hysteresis, be practically insensitive to acceleration effects, be capable of being flush-mounted, have a very small active



diaphragm area, have linear static and dynamic characteristics and one resonant frequency and output compatible for use with the electronic compensator ("DATTA") and other associated electronics, have a high resonant frequency, i. e., small rise time, to permit measurement of microsecond transient pressures, have a low damping ratio, have a range of approximately 0 to 10,000 psi with overload capabilities, have a high output signal, and be capable of static and dynamic calibration.

A number of different types of pressure transducers were tested to determine the one most suitable for use in this investigation. The two strain-gauge types tested (Norwood\* and Statham\*\*) were found to have too low a resonant frequency (approximately 30Kc/sec.) and therefore too large a rise time, to have excessively large effective diaphragm areas, to have small output signals, and to have rather low signal to noise ratios. In addition the Norwood had a catenary diaphragm, preventing flush-mounting. The variable reluctance type (Lane Wells \*\*\*) was capable of measuring rate of pressure only, had excessive "ringing", and had a low signal to noise ratio. The variable capacitance types (Rutishauser\*\*\*\* and Omega\*\*\*\*) had high frequency carrier circuits which were not sufficiently stable,

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\* Norwood Controls Div., -Detroit Controls, Norwood, Mass.

\*\* Statham Instruments, Inc., Los Angeles, Calif.

\*\*\* Lane Electronics Mfg. Co., North Hollywood, Calif.

\*\*\*\* Omega Instrument Co. (formerly Rutishauser Corp),  
Altadena, Calif.

and had too large a zero drift. The Brosa<sup>+</sup> (EBM) Model 6010 piezoelectric quartz type was found to have a relatively large diaphragm area, a relatively low predominant resonant frequency (60 Kc/sec.) and multiple degrees of freedom.

The Kistler SLM Model 605 miniature piezoelectric quartz crystal pressure pickup was found to have the most acceptable characteristics, i. e., small size, high voltage output, ruggedness, low damping ratio, high natural frequency and very close to a single degree of freedom. This transducer was chosen for use in this investigation. The transducer was supplied by the manufacturer according to specifications written specifically to permit undistorted measurements of the highly transient pressures encountered in detonation wave phenomena, when used in conjunction with the Dresser "DATTA" electronic compensator and associated electronic equipment. The transducer was an uncooled, flush-mounted design of stainless steel construction, capable of measuring pressures from 0 to 10,000 psi with a 50% short-time overload factor. The maximum error was guaranteed to be not more than 1/2% of full pressure range and not more than 2% at any point within the range. The pick-up was guaranteed to be insensitive to temperature transients up to 4500°K for a duration of 1 second and to be relatively insensitive to acceleration effects, i. e., axial acceleration sensitivity of 0.02 psi/g. The

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+ Elastronics Co., 19458 Ventura Blvd., Tarzana, Calif.

natural frequency of the transducer was about 133 Kc/sec., and the rise time was about 3 microseconds to a step increase in pressure. The output signal was about 0.5  $\mu\text{C}$  coulombs per psi or approximately 4000  $\mu\text{C}$  coulombs at full rated output. The transducer further had essentially linear static and dynamic characteristics and one-degree of freedom (i. e., one resonant frequency), and its output was characterized closely by a second order linear differential equation of the form:  $m\ddot{X} + c\dot{X} + kX = F(t)$ . This last requirement was necessary in order to insure optimum compatibility of the transducer with the Dresser "DATTA" electronic compensator. (See following section on Electronic Compensator for additional details).

The Kistler pressure transducer is essentially a capacitance-type transducer using a quartz crystal. Fig. 17 shows the internal construction of the transducer. The pressure sensitive element consists of two ground quartz crystals of semi-cylindrical shape with a steel electrode between them tightly compressed in a thin-walled stainless steel tube machined from a solid piece. Pressure is transmitted to the quartz crystals through axial loading of the solid end of the tube which is exposed to the pressure media. Deflection of the crystals produces a charge between their surfaces; i. e., the piezoelectric effect. A composite diaphragm prevents the introduction of spurious pressure signals due to thermal and mechanical

strains which may occur in the transducer housing during installation and during operation. Physically the pressure transducer is quite small, being 1/2-inch long and 1/4-inch in diameter and offering a small exposed area, approximately 1/8-inch in diameter. Fig. 18 is a photograph of the Kistler miniature pressure transducer, together with several of the other transducers tested.

### 3. Pressure Transducer Mount

Early in the detonation tests, it was observed that the output signal from the pressure transducer was modulated by low frequency signals approximating the natural frequency of the detonation tube. These spurious signals were attributed to acceleration effects on the transducer caused by "stress" or "ground waves" traveling through the metal tube walls ahead of the shock wave in the gas upon formation of the detonation wave. A number of different pressure transducer mounting designs, both rigid and isolation- or shock-mount types, were tested in order to obtain a mount which would minimize these acceleration effects. A photograph of several of the rigid and isolation-type mounts is given in Fig. 18. One of the types of "isolation"-mounts tested consisted of a metal plug retaining the transducer. The plug assembly was installed in the detonation tube wall. "O" rings were used to isolate it from direct contact with the wall as well as to shock mount and pressure seal it in the detonation tube. Another "shock"-mount design consisted of two cylindrical metal bushings

separated by a rubber bushing. The inner metal bushing retained the pressure pick up, and the outer metal bushing was rigidly mounted in the detonation tube. The shoulder of the outer bushing accommodated a rubber "O" ring for pressure- sealing the mount assembly in the detonation tube.

It was found that use of the isolation or shock-type mounts reduced somewhat the influence of the "ground waves" on the transducer output signal. However, it was found that good reproducibility of pressure measurements could not be obtained when using this type of mount. This was attributed to the fact that a portion of the energy imparted by the detonation wave was absorbed by the shock mounting or isolating material. The amount of energy absorption apparently was a function of the percentage of compression of the "O" rings or the amount of torque imparted to the assembly during installation in the detonation tube. No great difference in the form of the signal output from the transducer was observed in preliminary detonation tests, when using either the rigid-or the isolation-type transducer mounts. It was decided, therefore, to use the rigid type mounting design for retaining the pressure transducer.

In actual operation the pressure transducer was retained rigidly in a metal bushing which was screwed directly into the detonation tube wall. The bushing was designed so that the pressure sensing

surface of the transducer was perpendicular to the detonation tube axis and essentially flush with the inside wall of the tube. Pressure sealing was obtained through the use of a rubber "O" ring located in the shoulder of the bushing. A photograph of the pressure transducer, as well as one of the ionization probes, mounted in the detonation tube is given in Fig. 15. (See also Fig. 2.)

The effect of "ground waves" on the pressure transducer, although not eliminated by the use of the rigid-type mount, in most cases did not seriously affect the interpretation of the dynamic pressure oscilloscope traces obtained in the detonation tests. It is felt that almost complete elimination of such effects could have been attained had sufficient time been available to fabricate and check out several other shock-type mounts. One design in particular involved greatly increasing the effective mass of the pressure transducer by the addition of weights so as to reduce to a very low value the natural frequency of the pickup in the vertical mode of vibration. The design also involved the isolation of the pickup from the tube as well as pressure sealing by means of rubber "O" rings.

#### 4. Amplifier Calibrator

A Kistler Model 656 dual channel amplifier-calibrator and low noise high-resistance cable was used in conjunction with the Kistler

pressure transducer to match the extremely high internal impedance of the pickup (on the order of  $10^{14}$  ohms) to the impedance of the "DATTA" electronic compensator and to the oscilloscope. Each channel of the amplifier-calibrator consists basically of a series of switch-selected shunt input high-insulating capacitors to provide full output voltage for different input ranges or magnitudes of input electrostatic charge from the transducer; i. e., (5000, 1000, 5000 and 10,000 psi); an electrometer tetrode circuit; a four-stage transistorized amplifier directly coupled to the electrometer; and a precision calibrating voltage potentiometer.

In operation, the electrostatic charge signal, developed at the quartz crystal surface upon application of pressure, is received by the shunt input capacitor. The capacitor voltage is measured by the electrometer tube circuit. Since the overall input impedance, and therefore the overall leakage resistance of the electrometer circuit is in the order of  $10^{14}$  ohms, the charge is removed very slowly from the crystal. This contributes to the very long charge-time-constant of this system, on the order of hours, giving adequate time to complete a static calibration of the system. The four-stage transistorized amplifier is a push-pull unit with a voltage gain adjustable from 3 to 6 and an output impedance of less than 100 ohms. This is compatible with the "DATTA" and oscilloscope inputs. The amplifier calibrator used was modified by the manufacturer to have a frequency

response which was flat over the range of 0-200Kc, which is higher than the standard off-the-shelf unit (0-160Kc). The output sensitivity of the unit ranged from 0.25 to 7 mv/psi, depending on the input range selected; and the unit had a 1-percent linearity.

The amplifier-calibrator has circuitry incorporated to permit static and/or dynamic calibration of the pressure measuring system. The pressure measuring system was statically calibrated using both a dead-weight tester and high-pressure air. Also, it was dynamically calibrated using shock tube techniques. The instrumentation and techniques used to statically and dynamically pressure calibrate the pressure transducer, as well as to obtain dynamic characteristics of the transducer; i. e., natural frequency and damping factor, are discussed in Appendix VII B.

## 5. Oscilloscope

The pressure transducer output was displayed on a Tektronix type 535 oscilloscope using a Tektronix type 53C D. C. -coupled pre-amplifier plug-in unit. The sensitivity range of the preamplifier is 0.05 to 20V/cm, and the rise time of the unit is approximately 0.4 microseconds. The frequency response of the scope and plug-in unit is D. C. to 8.5 MC. Calibrated time sweeps over a wide range of values are provided; i. e., from 10 microseconds to 2 minutes total



sweep durations. The sweep speed was triggered by an external signal generated by the circuit described in the section on dynamic calibration of the pressure measuring system. (See Appendix VIIB-2.) Permanent records of the pressure transducer response were obtained using a DuMont Model 302 oscilloscope camera with a Polaroid Land camera back.

#### 6. Electronic Compensator

The Dresser Model "DATTA" (Dynamic Analog Transistorized Transducer Analyzer) electronic compensator is essentially a high-speed on-line analog computer, integrally incorporated as part of the pressure measuring system. It is designed to correct automatically transducer dynamic errors during actual transient and steady-state measurements. The compensator is designed to take the first and second derivatives of the transducer output, multiply by appropriate constants, and deliver an output voltage proportional to the original driving pressure. That is, the compensator inserts an active equalizing circuit or transfer function into the pressure measuring system which is exactly the inverse of the transfer function of the transducer. The operation performed by the compensator in an analog computer fashion is

$$m\ddot{X} + C\dot{X} + kX = F(t) = y \quad (\text{AVI-1})$$

The method used to perform these computations is shown functionally in the block diagram of Fig. 19. The above second order linear differential equation describes the dynamic behavior of an electro-mechanical pressure transducer with essentially linear characteristics having one degree of freedom (78). In this equation " $m^*$ " is the effective mass of the transducer, " $C$ " is the damping coefficient, " $k$ " is the spring constant of the transducer's elastic, " $X$ " is the voltage output of the transducer proportional to the displacement of the transducer diaphragm, and  $F(t) = y$  is the driving function acting on the transducer diaphragm area. (The Kistler SLM pressure transducers used in these investigations were found to have essentially linear characteristics and one degree of freedom characterized by the differential equation given above.)

From vibration theory (302)

$$k/m^* = \omega_0^2 \quad \text{and} \quad 2\sqrt{km^*} = C_r \quad (\text{A VI}-2)$$

where  $\omega_0$ , the angular undamped natural frequency of the transducer and  $C_r$  is the critical damping coefficient. Substituting from Eq. AVI-2 into Eq. AVI-1 and letting  $C/C_r = 2d$ , Eq. AVI-1 becomes

$$\frac{1}{\omega_0^2} \ddot{X} + \frac{2d}{\omega_0} \dot{X} + X = F(t)/k = f(t) \quad (\text{A VI}-3)$$

where  $d$  is defined as the damping ratio. Equation AVI-3 can thus be expressed in the following form:

$$A\ddot{X} + B\dot{X} + X = F(t)/k = f(t) \quad (\text{AVI-4})$$

By solving this equation electronically for  $F(t)$ , the "DATTA" theoretically can extend the undistorted frequency response of the system to approximately ten times the transducers natural resonant frequency.

The output of the "DATTA" system can best be analyzed on a frequency and phase basis, since it is designed to equalize the transducer response. Assuming the response of the transducer is described by a second-order linear differential equation, its frequency and phase response characteristics for a damping ratio of 0.1 are as represented in Fig. 20. For comparison, the phase and amplitude response curves of the "DATTA" system are also shown. The responses are exactly opposite to that of the transducer. The combined effect of the transducer and "DATTA" responses is to make the net response curve essentially flat through and far beyond the resonant frequency of the transducer. The upper limit of the frequency response of the "DATTA" system is dependent on the electronic amplifier limitations and particularly on the noise level of the transducer output. Therefore, Fig. 20 is only a functional representation. It can be seen from Fig. 20 that at frequencies above the transducer's natural frequency, the gain of the system increases in order to equalize the transducer's attenuation.

Therefore, any high-frequency noise is also amplified, interfering with the output signal. Thus for optimum results, the signal from the transducer should have a high signal-to noise ratio. Figure 21 is a functional representation (oscillogram) of the response of the "DATTA" pressure measuring system using an idealized simulated transducer, i. e., an electrical analog transducer, with the same transfer function as an electromechanical transducer described by a second-order linear differential equation. Represented are the driving voltage, the transducer analog circuit response, the first derivative, and the sum of the latter three, which is the reconstruction of the original driving function. Shown in Fig. 22a are another driving function (a 3-microsecond square wave pulse of less than 0.1 sec. rise time), the resultant simulator transducer response, and the reconstructed driving function; i. e. equalized "DATTA" output. A sweep expansion to show details is given in Fig. 22b. From Fig. 22b, the reconstructed pulse has a rise time of about 0.5 microseconds and a delay of approximately the same amount. Thus under idealized conditions, the pressure measuring system used in this investigation has the capabilities of observing transients with rise time on the order of 0.5 microseconds when used with transducers of sufficiently high natural frequencies. In the check-out tests of the pressure measuring system, it was found that the amplifier-calibrator electrometer tube produced some random noise in the 1 Mc to 20 Mc region; i. e., thermionic noise. This noise was greatly amplified when

the output signal was sent to the "DATTA" electronic compensator, interfering with its signal output and preventing good interpretation of the oscilloscope traces. Thus a 150 KC low-pass output filter, incorporated as part of the "DATTA" input circuitry, had to be used in most cases. The rise time for the entire pressure measuring system (pressure transducer, amplifier-calibrator, "DATTA", and oscilloscope) under these conditions was about 3 microseconds.

In order to enter the proper multiplying constants into the "DATTA" electronic compensator so that the driving function could be computed electronically, it was necessary to determine the undamped natural frequency,  $f_0$ , the damping ratio,  $d$ , ("d" for a fast response dynamic transducer is largely limited to internal damping and is usually small), and the value of the spring constant,  $k$ , for the particular pressure transducer to be used. The value of the spring constant,  $k$ , can be obtained accurately through static calibration, both before and after the dynamic tests. In this investigation static calibration of the Kistler SLM pressure transducer was performed using a dead weight tester and high-pressure air as the sources of pressure. Discussion of the static calibration instrumentation and techniques is given in Appendix VIIA. Results of the static calibration are shown in Fig. 25.

The natural frequency and damping ratio as well as the rise time can be determined by a number of well established methods. (34, 78, 204, 207, 208, 291, 302) One of the most convenient and new generally accepted standard methods for obtaining this information is to excite

the mechanical system of the pressure pickup at its natural frequency by means of the clean and sharp step function in pressure generated in a shock tube. The desired transducer dynamic characteristics can be calculated from the transducer transient response signal, i. e., oscillatory pattern of the system following the initial rise.

A 2 1/2-inch inside diameter shock tube was used to obtain the dynamic characteristics of the pressure transducers used in this investigation. A description of the instrumentation and techniques and presentation of the theoretical equations used in the shock tube calibration is given in Appendix VIIB. A photograph of the shock tube and associated instrumentation is shown in Fig. 23. Figure 24 is a typical photograph of the transient response output due to the shock pressure step excitation of one of the Kistler SLM Model 605 pressure transducers used in conjunction with the Kistler Model 656 amplifier-calibrator, as displayed on a direct-coupled Tektronix 535 oscilloscope and recorded on a Polaroid land camera. From this trace the undamped natural frequency of the transducer ( $f_0$ ) was found to be approximately 133 Kc, and the damping ratio ( $2d$ ) was found to be approximately 0.026. (See Appendix VIIB.)

The "DATTA" unit was provided with an input amplifier gain control switch which was adjustable in four ranges; 0.5, 0.2, 0.1 and 0.05 (low range); a damping ratio ( $2d$ ) control, continuously variable from 0 to 2; a frequency selector switch (high and low range); and a frequency

control ( $f_0$ ) continuously adjustable from 2KC to 20 KC (low range) to 20 KC to 300 KC (high range). The upper frequency range of the DATTA is 1.5 MC. A low pass output filter of 150 KC was provided to limit the upper frequency response when higher frequency noise was present.

It was initially planned to attempt to measure the pressure existing in the postulated "von Neumann spike" or non-reacting shock front of the detonation wave. However, after considerable investigation, it is the opinion of this investigator that no pressure measuring system available today has response characteristics fast enough to permit accurate measurement of pressure over such an extremely short interval of time; i. e., a few mean free paths for the shock front and less than 0.1 microseconds for the detonation wave front and reaction zone for mixtures at 1 atmosphere or higher initial pressure. (See Literature Review, Section II-E, p. 36, and Section IV-B, p. 91 of this dissertation for details). Thus pressure measurements in this investigation were confined primarily to measurements of the pressure existing in the region following the completion of chemical reaction in the detonation; i. e., the Chapman-Jouguet pressure. At the Chapman-Jouguet point sufficient residence time is available to permit measurements of pressure with

existing instrumentation.

Also in this investigation the range of initial conditions over which pressure measurements could be made was limited by the physical properties of the pressure transducers available, as well as the response characteristics of the transducer and associated electronics. The experimental program was initially formulated to measure Chapman-Jouguet detonation pressures of stoichiometric hydrogen-oxygen additive mixtures at initial pressures up to 20 atmospheres. The pressure limitation was based on the assumption of a detonation pressure rise of 20 to 1 at the Chapman-Jouguet point and a multiplication factor of 1.5 due to the reflected wave, or an overall pressure ratio of 30 to 1. It was considered further that any pressure in excess of the Chapman-Jouguet pressure, such as that predicted for the "von Neumann spike" or that occurring during transition from deflagration to detonation, would be of such short duration that it would not affect the pressure transducer. Also it was thought that the duration of the transient high temperature in the shock front and reaction products would be short enough so that it would not affect the pickup. Thus, based primarily on the pressure ratio of 30 to 1, the available 10,000 psi Kistler pressure transducers should have been able to withstand the pressure imparted from a detonation wave originating



in stoichiometric hydrogen-oxygen-additive mixtures at initial pressures up to 20 atmospheres.

Early detonation tests proved that some of the assumptions made were not realistic. One of the Kistler pressure transducers was badly damaged when pressure measurements were attempted in pure stoichiometric hydrogen-oxygen mixtures at initial pressure of about 10 atmospheres. It appeared that the damage was caused more by temperature effects; i. e., hot product gas contact, than by pressure effects. The pickup face was eroded, the composite diaphragm was bubbled; and the pickup could no longer be statically calibrated. In order to prevent the loss of an additional (and last) pressure transducer, all detonation tests involving the measurement of detonation pressures were restricted to a maximum of 5 atmospheres initial pressure.

#### F. Experimental Technique

Prior to each test run, all loose carbon, water and other material accumulated from the previous run were removed from the tube by swabbing, to avoid possible influence of the contaminants on the measured detonation velocity and pressure. The tube was then dried thoroughly with high-pressure dry air. A minimum of 20 tube volumes of the premixed gas of the desired composition were

then permitted to flow through the tube during the detonation tube loading to insure that the tube was filled with the proper mixture. Final adjustment was then made of the initial pressure; the detonation tube was sealed off; and the mixing chamber and gauge manifold were vented. The electronic chronograph system was internally checked to insure that the 100 KC and the 10 MC signals were counting properly. Artificially generated signals, which simultaneously started and stopped all counters then were used to check and adjust the start and stop triggering levels on each counter to insure that the times indicated on all units agreed to within  $\pm 0.1$  microsecond. Finally, the entire chronograph system was checked out using a bank of externally mounted ionization probes and simulating the actual test run by starting all counters and then stopping each one in turn by shorting out the appropriate probe electrode.

Before each series of detonation test runs, the various components of the pressure measuring system were adjusted. The range and dial scale settings for the Kistler amplifier-calibrator were made. The resonant frequency and damping coefficient of the Kistler SLM 605 pressure transducer, obtained from dynamic calibration described in Appendix VII-B, as well as the proper gain were set on the "DATTA unit"; and the Tektronik 535 oscilloscope attenuation was adjusted until the desired beam deflection was obtained. Preliminary to each run, the pressure transducer and

associated electronics were rechecked by the application of static high-pressure air to the transducer and comparing the pressure reading obtained from the oscilloscope trace to the pressure indicated on a precision Heise gauge. In this manner, the internal calibration system, described in more detail in Appendix VII-A, was checked. As an additional check of the pressure measuring system, each series of pressure measurements were preceded and followed by measurements on a "standard" system, stoichiometric hydrogen-oxygen. Comparison of these "standard" measurements served to indicate whether the dynamic response of the pressure measuring system remained constant.

After final adjustment of the amplifier-calibrator, the "DATTA" and the oscilloscope, the pressure transducer and the input to the electrometer of the amplifier-calibrator unit were manually grounded until the checks on the velocity measuring system were completed and the detonation tube was loaded and sealed off. To minimize drift due to charge build-up on the pressure transducer, the pressure transducer and electrometer input were switched from ground approximately one second before ignition of the detonable mixture.

Following the checkout of the velocity and pressure measuring

systems, voltage was applied to the ionization probes the pressure transducer and electrometer input were switched from ground, and the oscilloscope camera was set. The 5000-volt power supply was then momentarily impressed across the exploding wire igniter to initiate the detonation. The time required for the propagation of the detonation wave between each of the five ionization probe stations was displayed on the four 10 MC time interval units. The average detonation velocity was obtained directly by dividing the probe spacing by the time interval indicated on the counters. The oscilloscope's vertical deflection, produced by the pressure transducer output resulting from the pressure in the detonation wave, after being compensated by the "DATTA" unit, was photographed by the oscilloscope camera. The pressure of the Chapman-Jouguet region was then determined directly by examination of the photograph in conjunction with static and dynamic calibration data on the pressure transducer (See Fig. 25).

## APPENDIX VII

### INSTRUMENTATION AND TECHNIQUES FOR CALIBRATION OF PRESSURE MEASURING SYSTEM

#### A. Static Calibration

The amplifier-calibrator contains a precision source of electrostatic charge, the magnitude of which is controlled by a large dial, calibrated directly in psi, and a calibration button on the panel. These pulses of known voltage amplitude at the input to the electrometer simulate an actual transducer voltage and are used to facilitate static calibration of the pressure measuring system. In the manufacturer's description of the static calibration, the charge generated by a known pressure is exactly neutralized by a charge applied to the calibrating "capacitor" in the amplifier-calibrator from a constant voltage source by means of a built-in precision potentiometer. In this case the electrometer amplifier, together with the "DATTA" and an oscilloscope directly coupled to the calibrator output, act as a null indicator only, with the resultant calibration being in terms of psi/dial division or total psi. The calibration is carried out with the ammeter on the amplifier-calibrator set accurately at 1.00 milliamperes in order to fix the gain of the pre-amplifier as well as the voltage applied to the calibration potentiometer. An internal gain control potentiometer was provided in the electrometer circuit to permit adjustment of the electrometer output voltage so that agreement could be obtained between the signal output

voltage, as observed by the vertical deflection on the oscilloscope, from both the static pressure source and from the simulated pressure calibration source incorporated in the amplifier calibrator circuitry. This calibrating voltage could then be used at any time to check the sensitivity of the transistor amplifier, the electronic compensator, or the oscilloscope.

In the pressure measuring system used in this investigation, the pickup voltage output signal, after passing through the amplifier-calibrator and "DATTA" electronic compensator, was sent to a Tektronic 535 oscilloscope. The amount of vertical deflection of the oscilloscope beam produced by a given pressure impulse was therefore dependent upon the range and scale settings of the electrometer, the gain of the "DATTA," and the attenuator setting of the oscilloscope. The "DATTA" gain and the oscilloscope attenuation controls were adjusted so that the oscilloscope deflection observed when the electrometer "Calibrate" button were depressed; i. e., simulated pressure transducer voltage output used, could be interpreted directly in terms of psi/cm of beam deflection. The main limitation on the accuracy of the pressure readings was the restricted ( 6 cm. ) deflection available with the oscilloscope beam.

It was found necessary to perform a calibration on each transducer and amplifier-calibrator channel as a set in order to obtain

an accurate applied pressure change to dial setting relationship. Since in the present investigation, it was necessary to cover a wide range of pressures, it was decided to use a single pressure transducer with both channels of the amplifier-calibrator. Thus one of the channels was calibrated for the range 0-1000 psi while the other channel was calibrated for the range 0-5000 psi. In each case, the electrometer circuit gain was adjusted so that the calibrated dial read directly in psi. In this manner a series of pressure measurements could be made with the same pickup simply by switching electrometer channels, without the necessity of internal gain changes or recalibration of a single channel for different ranges.

The pressure pickup combination was statically calibrated in terms of psi, obtained directly from the large calibration dial on the calibrator; i. e., calibration factor of unity. For the initial static calibrations of the pressure measuring system, a dead weight tester was used to supply pressure to the pickup over a range of 0-5000 psi, with an accuracy of  $\pm 0.3\%$  of the pressure. For all subsequent calibrations and rechecks of the pressure pickup and associated electronics, static high-pressure air was applied to the pickup in parallel with a Heise precision gauge, accurate to  $\pm 3$  psi. throughout the range of 0-3 000 psi. These static rechecks were accomplished prior to each detonation test and after each series of

tests to insure that the pressure reading obtained from the oscilloscope trace agreed with that indicated on the Heise gauge. Pressure was applied to the pressure transducer in about ten steps over the pressure range. Fig. 25 shows a plot of the static calibration of one of the pressure transducers used in conjunction with the "DATTA" electronic compensator, the oscilloscope, and both channels of the amplifier-calibrator.

## B. Dynamic Calibration

### 1. General

The dynamic characteristics of the Kistler SLM pressure transducer; i. e., resonant natural frequency and damping factor, and dynamic pressure calibration of the transducer were obtained through the use of shock tube techniques. A block diagram of the system used to calibrate the pressure transducer is shown in Fig. 26. Fig. 23 is a photograph of the shock tube and associated instrumentation used. The shock tube used for the calibration work was a 2-1/2 inch inside diameter (3/4-inch wall) steel tube approximately 6-feet long. Aluminum diaphragms were used to separate the driver and driven sections. The aluminum diaphragms were scored to insure that the shock front produced would be planar. Two identical Kistler SLM pickups were flush-mounted in the side of the shock tube perpendicu-



lar to the tube axis, the faces of the transducers being flush with the inner wall of the tube. The distance between the two pickups was 2-feet. The first pickup was located 3-feet from the upstream end of the driver section (See Fig. 26). The step function in pressure was provided by rupture of the scored aluminum diaphragm. The rupture was accomplished by slowly increasing the pressure in the driving chamber normally supplied by high-pressure air.

## 2. Dynamic Characteristics of Pressure Transducer

The electronic instrumentation used to obtain the dynamic characteristics of the pressure transducer was essentially the same as that used for the static calibration, (See Appendix VIIA) except that the "DATTA" electronic compensator was not used. Thus the electronic instrumentation consisted essentially of the pressure pickups, the dual-channel amplifier-calibrator, the oscilloscope, and the Polaroid Land camera.

In the actual calibration tests, the first pressure transducer signal, obtained in passage of the shock front, was used to trigger the oscilloscope sweep. The signal output of the second transducer; i. e., the transducer undergoing calibration, was sent through low-noise high-resistance cables to the amplifier-calibrator. From there the signal went to the oscilloscope, where the transient response

output of the transducer was displayed on the oscilloscope and recorded on the Polaroid Land camera (See Fig. 24).

From this trace the dynamic characteristics of the Kistler SLM pressure transducers were determined through use of the following analysis (207, 208, 291). The transducers' natural frequency with damping ( $f_d$ ) can be determined from the following relationship (207, 208, 291):

$$f_d = \frac{\text{no. cycles}}{\text{time interval}} = \frac{n}{t} ; \quad (\text{AVII-1})$$

and from Eq. (AVII-1), the undamped natural frequency ( $f_0$ ) can be calculated by the equation:

$$f_0 = \frac{f_d}{[1-d^2]^{1/2}} \quad (\text{AVII-2})$$

The damping ratio ( $d$ ) of the system can be determined from the measured logarithmic decrement of the number of cycles ( $n$ ) in one time constant ( $t_c$ ), where  $t_c$  is the time it takes for the signal to decay to  $\frac{1}{e}$  of its original value ( $e = 2.718$ ).

$$t_c = \frac{1}{d\omega_0} = \frac{1}{2\pi f_0 d} \quad (\text{AVII-3})$$

$$t = nT = \frac{n}{f_n} \quad (\text{AVII-4})$$

where  $T = \frac{1}{f} = \frac{1}{f_d}$  = Period of one cycle.

Setting  $t = t_c$  and counting the number of cycles in one time constant, then

$$\frac{n}{f_d} = \frac{(1-d^2)^{1/2}}{2\pi f_d d} \quad (\text{AVII-5})$$

and

$$2d = \frac{1}{\pi n \left(1 + \frac{1}{4\pi^2 n^2}\right)^{1/2}} \quad (\text{AVII-6})$$

For values of  $n > 3.6$ , the following formula may be used with less than 0.1% error:

$$2d = \frac{1}{\pi n} \quad (\text{AVII-7})$$

From Eq. (AVII-2), the undamped natural frequency,  $f_0$ , can now be determined. For values of  $d < 0.045$ ; i. e., small damping, the difference between  $f_0$  and  $f_d$  will be less than 0.1%; and for all practical purposes  $f_0 = f_d$ :

From the transient response output of the pressure transducer, (See Fig. 24), and utilizing the above relationships, the undamped natural frequency of the transducer ( $f_0$ ) was found to be approximately 133 KC; and the damping factor ( $2d$ ) was found to be approximately 0.026.

### 3. Dynamic Pressure Calibration

The same shock tube set-up used for the determination of the dynamic characteristics of the pressure transducers was used for the dynamic pressure calibration of the transducers (See Appendix VII B-1 above). The instrumentation used was also the same but in addition included the "DATTA" electronic compensator, a Tektronix type 112 wide-band amplifier and a Hewlett-Packard 10MC electronic chronograph. (Refer to Fig. 26 for the block diagram of the calibration system, and see Appendix VI-D3 for description of the chronograph). Scored aluminum burst diaphragms of various thicknesses were used to obtain step functions of pressure ranging from about 50 psia to 100 psia in rise times of less than 1 microsecond. Air was used in both the driver and driven sections of the tube.

From the photograph of the deflected oscilloscope trace (See Fig. 27) and the static calibration of the pressure transducer, (See Fig. 25) the pressure sensed by the pressure transducer was computed. The magnitude of the shock pressure jump was computed from the measured values of the pressure and temperature in the driven (low pressure) section and the shock wave velocity. The shock wave velocity was determined from the transient time measured by the electronic chronograph for the shock to travel between the two fixed pressure transducers mounted a known distance apart in

the shock tube wall. Use was made of the following shock relationship: (4, 67, 128, 146, 205, 226)

$$\frac{p_2}{p_1} = \frac{2\gamma M_s^2 - (\gamma - 1)}{\gamma + 1} \quad (\text{AVII-8})$$

where  $M_s$  is the Mach number,  $\frac{u_1}{a_1}$  of the shock wave moving with constant velocity,  $u_1$ , into the gas at rest. The constant,  $\gamma$ , the heat capacity ratio, refers to the gas originally at rest in the driven section and " $a_1$ ", is the velocity of sound of the gas in the driven section. For air,  $\gamma = 1.4$  and Eq. (AVII-8) becomes:

$$\frac{p_2}{p_1} = \frac{7M_s^2 - 1}{6} \quad (\text{AVII-9})$$

Fig. 27 is a typical photograph showing the response of the Kistler SLM Model 605 pressure transducer amplifier-calibration and "DATTA" electronic compensator to shock wave pressure steps. Fig. 25 shows the comparison of the dynamic and static calibration of the pressure measuring system.

In the actual dynamic calibration tests, Kistler low-noise high-resistance cables connected the two Kistler pressure transducers to the Kistler dual-channel amplifier-calibrator. The damping coefficient and resonant frequency controls of the "DATTA" electronic compensator were set to compensate for the characteristics of the transducers being calibrated, as described in Section B1 of this

appendix. The output from the first transducer, obtained upon application of the shock front pressure step, was fed to one channel of the amplifier-calibrator. This signal, after additional amplification by the Tektronix 112 wide-band amplifier, was used to trigger the sweep of the oscilloscope recording the output of the second pressure transducer, the pickup being calibrated. In addition, this triggering signal was used as the start input for the 10 MC timer interval meters of the electronic chronograph.

The output signal from the second pressure transducer was sent to the second channel of the amplifier calibrator. The amplified signal was then taken to the input of the "DATTA" unit. From the "DATTA," the compensated transducer signal was fed to the Tektronix 535 oscilloscope, where it produced a vertical deflection proportional to the magnitude of the driving pressure function. The stop input for the 10 MC electronic chronograph was obtained from the vertical signal output of the oscilloscope.

Various investigators (194, 289) have shown that quartz crystal pressure transducers similar to those used in this investigation are essentially linear over their entire operating range and that dynamic pressure calibrations agree very well with static calibrations. It was not felt warranted, therefore, in view of the greater com-

plexities in equipment required, to attempt to extend the dynamic pressure calibration beyond the range reported here. It was assumed, therefore, that the dynamic and static calibration curves are the same over the entire pressure range of the pressure pickup. It was felt that this should be very close to an actuality due to the small mass and therefore the small inertia effect of the pickup.

**Appendix VIII.**  
**Theoretically Calculated Detonation Parameters**



TABLE 1. CALCULATED DETONATION PARAMETERS FOR  $H_2 - O_2$  MIXTURES  
 $2H_2 + O_2$   
 66 2/3 %  $H_2$  IN THE BASIC (STOICHIOMETRIC)  $H_2 - O_2$  MIXTURE (BY VOLUME)  
 INITIAL TEMPERATURE 300° K  
 $n' = 3$  GM. MOLES  $m' = 12.0067$   $\gamma' = 3.49133$   $c_{H_2} = 539.4878$  METERS PER SEC

DETONATION PARAMETERS	INITIAL PRESSURE, ATMOSPHERES						
	0.5	1	5	10	20	100	1000
$T^*$ DEG K	3.53967E 03	3.66669E 03	3.98279E 03	4.12665E 03	4.27629E 03	4.62321E 03	5.10200E 03
$P^* / P'$	1.81126E 01	1.85444E 01	1.96059E 01	2.00532E 01	2.05102E 01	2.15030E 01	2.26094E 01
$\rho^* / \rho'$	5.43878E-01	5.44828E-01	5.45833E-01	5.46808E-01	5.47720E-01	5.47682E-01	5.47224E-01
$\rho'$ GM / CM <sup>3</sup>	2.43959E-04	4.87917E-04	2.43959E-03	4.87917E-03	9.75834E-03	4.87917E-02	4.87917E-01
$m' / m^*$	1.19773E 00	1.20970E 00	1.24057E 00	1.25520E 00	1.27040E 00	1.28075E 00	1.28494E 00
D METERS / SEC	2.79136E 03	2.82934E 03	2.91609E 03	2.95387E 03	2.98995E 03	3.06796E 03	3.16115E 03
$M'$	5.17613E 00	5.24456E 00	5.40677E 00	5.47532E 00	5.54382E 00	5.68681E 00	5.89954E 00
$P^*$ ATMOS	1.57320E 01	3.22820E 01	1.70436E 02	3.40649E 02	7.13716E 02	3.74614E 03	3.94910E 04
$n'$ GM MOLES	2.50473E 00	2.47996E 00	2.41025E 00	2.39004E 00	2.36109E 00	2.29224E 00	2.19709E 00
$x_{H_2}^*$	8.69330E-02	7.91704E-02	6.13616E-02	5.30979E-02	4.67250E-02	3.16820E-02	1.69766E-02
$x_{O_2}^*$	1.65344E-01	1.63092E-01	1.55330E-01	1.50714E-01	1.45177E-01	1.29044E-01	9.91329E-02
$x_{H_2O}^*$	5.22857E-01	5.36868E-01	5.72644E-01	5.91212E-01	6.11591E-01	6.65630E-01	7.52069E-01
$x_{CO}^*$	4.04500E-02	3.76937E-02	3.01723E-02	2.69170E-02	2.36676E-02	1.64391E-02	8.11651E-03
$x_{CO_2}^*$	5.07675E-02	4.87273E-02	4.57231E-02	4.14090E-02	3.69671E-02	3.30240E-02	2.49587E-02
$x_{OH}^*$	4.76211E-06	1.07531E-07	3.63042E-07	4.62047E-07	6.90877E-07	1.68160E-06	5.21067E-06
$Y_{H_2}^*$	1.33639E-01	1.35457E-01	1.36779E-01	1.35049E-01	1.33871E-01	1.24576E-01	1.00766E-01
$Y_{O_2}^*$	1.22094E 00	1.21717E 00	1.20829E 00	1.20442E 00	1.20056E 00	1.19180E 00	1.18080E 00
$Y_{H_2O}^*$	1.22179E 00	1.22063E 00	1.21733E 00	1.21551E 00	1.21340E 00	1.20724E 00	1.19922E 00
$Y_{CO}^*$	1.12656E 00	1.13243E 00	1.14053E 00	1.14692E 00	1.14734E 00	1.15415E 00	1.16470E 00
$c_{H_2}^*$ METERS / SEC	1.50049E 03	1.59814E 03	1.63874E 03	1.65567E 03	1.67209E 03	1.70720E 03	1.76814E 03
$c_{O_2}^*$ METERS / SEC	1.51700E 03	1.53096E 03	1.58996E 03	1.61149E 03	1.63295E 03	1.67805E 03	1.73126E 03
$c_{H_2O}^*$ METERS / SEC	1.51017E 03	1.54151E 03	1.59213E 03	1.61425E 03	1.63461E 03	1.68002E 03	1.73610E 03
$u^*$ METERS / SEC	1.51022E 03	1.54155E 03	1.59210E 03	1.61430E 03	1.63460E 03	1.68007E 03	1.73623E 03
$u_{H_2}^*$	9.60603E-01	9.64590E-01	9.71500E-01	9.75017E-01	9.77615E-01	9.84109E-01	9.93109E-01
$u_{O_2}^*$	1.00075E 00	1.00169E 00	1.00141E 00	1.00176E 00	1.00129E 00	1.00121E 00	1.00097E 00
$u_{H_2O}^*$	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00
$P_{H_2}^* / P'$	3.10794E 01	3.19250E 01	3.39523E 01	3.48230E 01	3.56006E 01	3.75782E 01	3.99660E 01
$P_{O_2}^* / P'$	5.04391E 00	5.06509E 00	5.11164E 00	5.13003E 00	5.14750E 00	5.18396E 00	5.22440E 00
$T_{H_2}^*$ DEG K	1.04053E 03	1.09140E 03	1.99272E 03	2.05642E 03	2.07946E 03	2.17640E 03	2.29140E 03
$T_{O_2}^*$	4.13253E-01	4.12360E-01	4.10423E-01	4.09653E-01	4.08931E-01	4.07646E-01	4.05810E-01
$\phi_{H_2}^*$ ATMOS	7.50500E 01	1.56689E 02	8.42169E 02	1.73513E 03	3.57043E 03	1.09620E 04	2.03204E 05

TABLE 2. CALCULATED DETONATION PARAMETERS FOR $H_2 - O_2 - He$ MIXTURES $CH_2 + O_2 + 1/3 He$						
66.275 % $H_2$ IN THE BASIC (STOICHIOMETRIC) $H_2 - O_2$ MIXTURES (BY VOLUME) 10 % $He$						
INITIAL TEMPERATURE 300° K						
$n^* = 3 \frac{1}{3}$	GM. MOLES	$m^* = 11.26900$	$\gamma^* = 3.39820$	$a_0^* = 541.7292$	METERS	PER SEC.

DETONATION PARAMETERS		INITIAL PRESSURE, ATMOSPHERES									
		0.5	1	5	10	20	50	100			
T <sup>o</sup> DEG K		3.50130E 02	3.52470E 03	3.93010E 03	4.04040E 03	4.20040E 03	4.54270E 03	4.99453E 03			
P <sup>o</sup> / P <sup>o</sup>		1.01644E 01	1.05937E 01	1.06700E 01	2.01220E 01	2.05053E 01	2.15990E 01	2.20940E 01			
P <sup>o</sup> / P <sup>o</sup>		3.49932E -01	3.52570E -01	3.44017E -01	3.47740E -01	3.50300E -01	3.50627E -01	3.50926E -01			
P <sup>o</sup> ON / CM <sup>3</sup>		2.27692E -04	4.55306E -04	2.27692E -03	4.55306E -03	9.34372E -03	4.56306E -02	4.55306E -02			
M <sup>o</sup> / M <sup>o</sup>		1.10032E 00	1.10000E 00	1.21704E 00	1.23007E 00	1.34321E 00	1.27542E 00	1.32219E 00			
D METERS / SEC		2.09541E 03	2.0970E 03	2.09940E 03	2.04700E 03	2.14400E 03	2.19947E 04	2.29000E 03			
M <sup>o</sup>		3.13462E 00	3.22610E 00	3.50130E 00	3.64130E 00	3.52720E 00	3.67710E 00	3.59320E 00			
P <sup>o</sup> ATMOS		1.57324E 01	3.22030E 01	1.70706E 02	3.49232E 02	7.14300E 02	3.74707E 03	3.46400E 04			
P <sup>o</sup> ON MOLES		2.00013E 00	2.77940E 00	2.73197E 00	2.70904E 00	2.60120E 00	2.61200E 00	2.52104E 00			
H <sub>2</sub>		7.57320E -02	4.75000E -02	3.70000E -02	4.50000E -02	3.50000E -02	2.50000E -02	1.20000E -02			
H <sub>2</sub> O		1.54037E -01	1.51607E -01	1.50675E -01	1.50400E -01	1.50400E -01	1.09540E -01	0.20090E -02			
CO		4.60220E -01	4.00040E -01	3.12010E -01	4.27240E -01	3.54047E -01	3.00070E -01	0.62700E -01			
CO <sub>2</sub>		1.00032E -01	1.10000E -01	1.01704E -01	1.02000E -01	1.02000E -01	1.07704E -01	1.02019E -01			
CH <sub>4</sub>		3.40130E -02	3.17777E -02	2.53090E -02	2.50000E -02	1.50000E -02	1.50000E -02	4.50000E -02			
C <sub>2</sub> H <sub>6</sub>		4.00000E -02	4.00000E -02	3.00000E -02	3.00000E -02	3.00000E -02	2.00000E -02	2.00000E -02			
C <sub>3</sub> H <sub>8</sub>		3.00000E -02	3.00000E -02	2.00000E -02	2.00000E -02	2.00000E -02	2.00000E -02	2.00000E -02			
OH		1.10000E -01	1.10010E -01	1.10000E -01	1.10700E -01	1.13000E -01	1.04090E -01	0.52090E -02			
Y <sub>CO</sub>		1.23000E 00	1.23010E 00	1.23030E 00	1.22200E 00	1.21070E 00	1.21000E 00	1.10070E 00			
Y <sub>CO<sub>2</sub></sub>		1.21220E 00	1.21210E 00	1.21130E 00	1.21000E 00	1.21000E 00	1.20900E 00	1.20100E 00			
Y <sub>H<sub>2</sub>O</sub>		1.15150E 00	1.15670E 00	1.14500E 00	1.15000E 00	1.15000E 00	1.14000E 00	1.17310E 00			
Y <sub>CO</sub> METERS / SEC		1.05100E 03	1.04990E 03	1.13300E 03	1.73100E 03	1.74970E 03	1.70900E 03	1.63300E 03			
Y <sub>CO<sub>2</sub></sub> METERS / SEC		1.17430E 03	1.17770E 03	1.09500E 03	1.07700E 03	1.70070E 03	1.75000E 03	1.61000E 03			
Y <sub>H<sub>2</sub>O</sub> METERS / SEC		1.57790E 03	1.60010E 03	1.65600E 03	1.60037E 03	1.70310E 03	1.75300E 03	1.61030E 03			
U <sup>o</sup> METERS / SEC		1.57790E 03	1.60010E 03	1.65600E 03	1.60037E 03	1.70310E 03	1.75300E 03	1.61030E 03			
W <sub>CO</sub>		0.50700E -01	0.50000E -01	0.64420E -01	0.70310E -01	0.73040E -01	0.60700E -01	0.50000E -01			
W <sub>CO<sub>2</sub></sub>		1.00000E 00	1.00150E 00	1.00000E 00	1.00130E 00	1.00100E 00	1.00150E 00	1.00130E 00			
W <sub>CO<sub>2</sub></sub>		1.00000E 00	1.00003E 00	1.00000E 00	1.00000E 00	1.00003E 00	1.00000E 00	1.00000E 00			
P <sub>CO</sub> P <sup>o</sup>		3.00930E 01	3.10620E 01	3.39107E 01	3.40103E 01	3.56912E 01	3.76562E 01	4.00010E 01			
P <sub>CO<sub>2</sub></sub> P <sup>o</sup>		4.00100E 00	4.00210E 00	4.00600E 00	4.00601E 00	5.00170E 00	5.03771E 00	5.07609E 00			
T <sub>CO</sub> DEG K		1.09403E 03	1.06190E 03	2.04071E 03	2.00490E 03	2.14070E 03	2.24040E 03	2.34030E 03			
T <sub>CO<sub>2</sub></sub>		4.10010E -01	4.17320E -01	4.15371E -01	4.09060E -01	4.13040E -01	4.12357E -01	4.10070E -01			
P <sub>CO<sub>2</sub></sub> (ATMOS)		7.85101E 01	1.51900E 02	6.75120E 02	1.40530E 03	3.47030E 03	1.00440E 04	0.17000E 05			

TABLE 3. CALCULATED DETONATION PARAMETERS FOR  $H_2 - O_2 - He$  MIXTURES  
( $2H_2 + O_2$ ) + He

66 2/3 %  $H_2$  IN THE BASIC (STOICHIOMETRIC)  $H_2 - O_2$  MIXTURE (BY VOLUME) 25 % He

INITIAL TEMPERATURE 300° K

$n' = 4$  GM MOLES  $m' = 12.00870$   $\gamma' = 1.24350$   $a_1' = 600.266$  METERS PER SEC

DETONATION PARAMETERS	INITIAL PRESSURE, ATMOSPHERES						
	0.5	1	2	10	20	100	1000
$T'$ DEG K	3.43103E 03	3.54877E 03	3.63344E 03	3.96162E 03	4.09170E 03	4.39397E 03	4.79944E 03
$P'$ / $P'$	1.01143E 01	1.05723E 01	1.06392E 01	2.00073E 01	2.05441E 01	2.15449E 01	2.27979E 01
$\rho'$ / $\rho'$	3.44907E -01	3.57527E -01	3.64394E -01	3.54940E -01	3.51250E -01	3.33275E -01	3.53487E -01
$\rho'$ GM / CM <sup>3</sup>	2.03295E -04	2.04590E -04	2.03295E -03	4.04590E -03	8.13100E -03	4.04590E -02	4.04590E -01
$m'$ / $m'$	1.15493E 00	1.14331E 00	1.10944E 00	1.19422E 00	1.20432E 00	1.22054E 00	1.26236E 00
$D$ METERS / SEC	3.06797E 03	3.11000E 03	3.21047E 03	3.25310E 03	3.27562E 03	3.30570E 03	3.49593E 03
$M'$	5.11059E 00	5.10041E 00	5.24079E 00	5.41957E 00	5.40040E 00	5.44051E 00	5.82400E 00
$P'$ ATMOS	1.56493E 01	1.59900E 01	1.64941E 02	3.46734E 02	7.09072E 02	3.71355E 03	3.92409E 04
$n'$ GM MOLES	3.44308E 00	3.43007E 00	3.37700E 00	3.25947E 00	3.25130E 00	3.25594E 00	3.10444E 00
$H_2$	5.61904E -02	5.64334E -02	5.81073E -02	3.30132E -02	2.01005E -02	1.02944E -02	8.20767E -03
$H_2$	1.13095E -01	1.10754E -01	1.03424E -01	9.93016E -02	9.47600E -02	8.10192E -02	6.01297E -02
$H_2O$	3.91770E -01	4.00013E -01	4.25533E -01	4.37045E -01	4.50052E -01	4.94700E -01	5.37204E -01
$He$	3.00713E -01	2.99027E -01	2.94114E -01	2.92544E -01	2.91000E -01	3.07139E -01	3.15521E -01
$H_2$	2.57133E -02	2.35443E -02	1.84123E -02	1.61975E -02	1.40227E -02	9.37047E -03	4.34919E -03
$H_2$	3.34024E -02	3.30040E -02	2.98724E -02	2.40579E -02	2.01062E -02	2.16345E -02	1.53947E -02
$H_2$	3.50299E -02	3.31094E -02	1.49090E -02	2.19310E -02	2.23207E -02	7.35454E -02	2.01300E -02
$H_2$	0.00170E -02	0.95440E -02	0.04355E -02	0.71511E -02	0.49337E -02	7.00652E -02	5.93291E -02
$Y_{H_2O}$	1.27834E 00	1.34679E 00	1.25430E 00	1.25447E 00	1.25107E 00	1.24343E 00	1.23310E 00
$W_{H_2O}$	1.20049E 00	1.20213E 00	1.20550E 00	1.20790E 00	1.20953E 00	1.21152E 00	1.21448E 00
$Y_{H_2O}$	1.13994E 00	1.14451E 00	1.15021E 00	1.16367E 00	1.16605E 00	1.16112E 00	1.19405E 00
$C_{H_2O}$ METERS / SEC	1.77090E 03	1.79161E 03	1.83934E 03	1.85950E 03	1.87914E 03	1.92101E 03	1.97279E 03
$C_{H_2}$ METERS / SEC	1.67513E 03	1.70124E 03	1.76167E 03	1.78764E 03	1.81529E 03	1.86990E 03	1.93940E 03
$C_{H_2O}$ METERS / SEC	1.67753E 03	1.70297E 03	1.76440E 03	1.79079E 03	1.81619E 03	1.87333E 03	1.94195E 03
$u'$ METERS / SEC	1.67753E 03	1.70302E 03	1.76473E 03	1.79095E 03	1.81624E 03	1.87339E 03	1.94201E 03
$M_{H_2O}$	9.47307E -01	9.50553E -01	9.59434E -01	9.63001E -01	9.66529E -01	9.74002E -01	9.84394E -01
$M_{H_2}$	1.00122E 00	1.00104E 00	1.00174E 00	1.00170E 00	1.00163E 00	1.00162E 00	1.00134E 00
$M_{H_2O}$	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00
$P_{H_2O}$	3.00993E 01	3.15490E 01	3.30414E 01	3.45412E 01	3.54332E 01	3.74314E 01	3.99105E 01
$P_{H_2}$	4.60264E 00	4.70153E 00	4.74311E 00	4.75903E 00	4.77549E 00	4.80000E 00	4.84595E 00
$T_{H_2O}$ DEG K	1.94401E 03	2.01444E 03	2.12700E 03	2.17704E 03	2.22505E 03	2.35510E 03	2.47125E 03
$M_{H_2}$	4.26271E -01	4.25379E -01	4.23435E -01	4.22661E -01	4.21931E -01	4.20410E -01	4.18741E -01
$P_{H_2O}$ ATMOS	6.95340E 01	1.43725E 02	7.74100E 02	1.54651E 03	3.20005E 03	1.75191E 04	1.00997E 05

TABLE 4. CALCULATED DETONATION PARAMETERS FOR  $H_2 - O_2 - He$  MIXTURES  
 $(2H_2 + O_2) + 1.8 He$   
 66.2/3 %  $H_2$  IN THE BASIC (STOICHIOMETRIC)  $H_2 - O_2$  MIXTURE (BY VOLUME) 37.5 %  $He$   
 INITIAL TEMPERATURE 300° K  
 $n' = 4.8$  GM MOLES  $m' = 9.007717$   $\gamma' = 3.11958$   $a_0' = 636.422$  METERS PER SEC

DETONATION PARAMETERS	INITIAL PRESSURE, ATMOSPHERES						
	0.5	1	5	10	20	100	1000
$T^*$ DEG K	3.35765E 03	3.44626E 03	3.72971E 03	3.84630E 03	3.96345E 03	4.23241E 03	4.57990E 03
$P^*/P'$	1.79732E 01	1.84250E 01	1.94421E 01	1.99001E 01	2.02920E 01	2.12407E 01	2.23704E 01
$\rho^*/\rho'$	5.48773E-01	5.42607E-01	5.52139E-01	5.53216E-01	5.54770E-01	5.37309E-01	5.00316E-01
$P^*$ GM/CM <sup>2</sup>	1.02963E-04	3.65926E-04	1.02963E-03	3.65926E-03	7.31853E-03	3.65926E-02	3.65926E-01
$m^*$ / m'	1.13463E 00	1.14135E 00	1.15014E 00	1.16574E 00	1.17356E 00	1.19100E 00	1.21625E 00
$D$ METERS / SEC	3.22734E 03	3.27259E 03	3.37609E 03	3.42036E 03	3.44401E 03	3.55020E 03	3.67157E 03
$M^*$	5.06557E 00	5.12603E 00	5.20945E 00	5.25804E 00	5.32590E 00	5.57344E 00	5.75110E 00
$P^*$ ATMOS	1.84441E 01	3.17174E 01	1.67004E 02	3.41200E 02	6.95509E 02	3.63186E 03	3.01100E 04
$n^*$ GM MOLES	4.23402E 00	4.20513E 00	5.14457E 00	4.11749E 00	4.09011E 00	4.02753E 00	3.94454E 00
$X_{H_2}^*$	4.10443E-02	3.72000E-02	2.73500E-02	2.34194E-02	1.97375E-02	1.24140E-02	5.31053E-03
$X_{O_2}^*$	0.01970E-02	0.09122E-02	7.90309E-02	7.53937E-02	7.13049E-02	6.04074E-02	4.29004E-02
$X_{He}^*$	3.27713E-01	3.34979E-01	3.54400E-01	3.64204E-01	3.76345E-01	4.02275E-01	4.34257E-01
$X_{H_2O}^*$	4.25420E-01	4.20007E-01	4.34303E-01	4.37159E-01	4.40004E-01	4.44924E-01	4.54493E-01
$X_{CO}^*$	1.00010E-02	1.79917E-02	1.34410E-02	1.13204E-02	9.40237E-03	4.26444E-03	2.74932E-03
$X_{CO_2}^*$	2.00210E-02	2.00014E-02	2.32701E-02	2.37940E-02	2.41121E-02	1.63204E-02	1.10722E-02
$X_{H_2O_2}^*$	2.13335E-00	3.31444E-00	0.00794E-00	1.30371E-07	1.00400E-07	4.13214E-07	1.01007E-06
$X_{OH}^*$	6.00423E-02	6.01051E-02	6.63946E-02	6.67303E-02	6.25319E-02	5.53015E-02	4.12632E-02
$y_{H_2}^*$	1.30232E 00	1.29990E 00	1.29005E 00	1.28763E 00	1.28400E 00	1.27649E 00	1.26772E 00
$y_{O_2}^*$	1.10462E 00	1.10759E 00	1.20500E 00	1.20053E 00	1.21204E 00	1.22039E 00	1.23150E 00
$y_{He}^*$	1.10461E 00	1.15312E 00	1.14943E 00	1.17593E 00	1.18463E 00	1.19944E 00	1.21099E 00
$u_{H_2}^*$ METERS / SEC	1.00403E 03	1.00021E 03	1.05090E 03	1.00014E 03	2.00077E 03	2.04575E 03	2.09900E 03
$u_{O_2}^*$ METERS / SEC	1.70443E 03	1.79739E 03	1.04243E 03	1.09030E 03	1.91795E 03	1.97947E 03	2.05531E 03
$u_{He}^*$ METERS / SEC	1.77125E 03	1.79794E 03	1.04449E 03	1.09244E 03	1.92173E 03	1.98304E 03	2.05915E 03
$u^*$ METERS / SEC	1.77131E 03	1.79800E 03	1.04455E 03	1.09251E 03	1.92179E 03	1.98312E 03	2.05921E 03
$M_{H_2}^*$	9.39161E-01	9.42244E-01	9.51037E-01	9.55740E-01	9.60523E-01	9.69304E-01	9.81622E-01
$M_{O_2}^*$	1.00095E 00	1.00034E 00	1.00114E 00	1.00115E 00	1.00200E 00	1.00104E 00	1.00100E 00
$M_{He}^*$	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00
$P_{H_2}^*$	3.02444E 01	3.11000E 01	3.31277E 01	3.40012E 01	3.46490E 01	3.60041E 01	3.91972E 01
$P_{O_2}^*$	4.49302E 00	4.51135E 00	4.54900E 00	4.56514E 00	4.57974E 00	4.61000E 00	4.64396E 00
$T_{H_2}^*$ DEG K	2.01919E 03	2.06016E 03	2.10434E 03	2.23440E 03	2.26410E 03	2.39542E 03	2.53215E 03
$T_{O_2}^*$	4.33634E-01	4.32754E-01	4.30043E-01	4.30007E-01	4.29371E-01	4.27093E-01	4.26264E-01
$P_{H_2O}^*$ ATMOS	6.57140E 01	1.35794E 02	7.30072E 02	1.50455E 03	3.10230E 03	1.05044E 04	1.77307E 05

TABLE 5. CALCULATED DETONATION PARAMETERS FOR  $H_2 - O_2 - He$  MIXTURES  
 $(2H_2 + O_2) + 3 He$   
 66.2/3 %  $H_2$  IN THE BASIC (STOICHIOMETRIC)  $H_2 - O_2$  MIXTURE (BY VOLUME) 50 %  $He$   
 INITIAL TEMPERATURE 300° K  
 $n' = 6$  GM MOLES  $m' = 8.006733$   $\gamma' = 2.99567$   $a_1 = 683.0095$  METERS PER SEC

DETONATION PARAMETERS	INITIAL PRESSURE, ATMOSPHERES					
	0.5	1	5	10	20	100
$T''$ DEG K	3.25704E 03	3.36492E 03	3.58710E 03	3.68920E 03	3.78950E 03	4.01384E 03
$\rho'' / \rho'$	1.76340E 01	1.60623E 01	1.49300E 01	1.43512E 01	1.37200E 01	2.05941E 01
$\rho' / \rho''$	5.52390E -01	5.53894E -01	5.57619E -01	5.58704E -01	5.59762E -01	5.6217E -01
$\rho'$ GM / CM <sup>3</sup>	1.62631E -06	3.25263E -06	1.62631E -05	3.25263E -05	6.50526E -05	3.25263E -04
$m'' / m'$	1.11405E 00	1.12002E 00	1.13273E 00	1.13820E 00	1.14300E 00	1.17273E 00
$D$ METERS / SEC	3.44223E 03	3.46777E 03	3.55251E 03	3.59746E 03	3.62222E 03	3.64110E 03
$M'$	4.97603E 00	5.04201E 00	5.19636E 00	5.26000E 00	5.32353E 00	5.61699E 00
$P'$ ATMOS	1.56600E 01	3.07953E 01	1.60702E 02	3.20706E 02	6.40743E 02	3.67167E 03
$n''$ GM MOLES	3.44100E 00	3.45733E 00	3.52493E 00	3.57113E 00	3.61627E 00	3.10753E 00
$X''_H$	2.7771E -02	2.69526E -02	1.72079E -02	1.65639E -02	1.60230E -02	7.19646E -03
$X''_{H_2}$	6.39704E -02	6.10160E -02	5.55199E -02	5.23769E -02	4.89693E -02	6.01066E -02
$X''_{H_2O}$	3.49772E -01	3.73513E -01	2.90822E -01	2.77704E -01	3.05340E -01	3.23900E -01
$X''_{He}$	5.57930E -01	5.60812E -01	5.66366E -01	5.69130E -01	5.71942E -01	5.78399E -01
$X''_O$	1.22299E -02	1.10131E -02	6.66970E -03	6.00922E -03	5.76679E -03	3.54767E -03
$X''_{O_2}$	2.67872E -02	1.96204E -02	1.67514E -02	1.54050E -02	1.42093E -02	1.12326E -02
$X''_{CO}$	1.15277E -02	1.75970E -02	4.42043E -02	6.42302E -02	9.10000E -02	1.66355E -01
$X''_{CO_2}$	4.79762E -02	4.75737E -02	4.51824E -02	4.35770E -02	4.15660E -02	3.55666E -02
$\gamma''$	1.34130E 00	1.33809E 00	1.33076E 00	1.32770E 00	1.32471E 00	1.31831E 00
$\gamma''_{H_2}$	1.19624E 00	1.19912E 00	1.21160E 00	1.21762E 00	1.22374E 00	1.23053E 00
$\gamma''_{H_2O}$	1.16340E 00	1.17040E 00	1.19309E 00	1.19859E 00	1.20705E 00	1.22571E 00
$\gamma''_{H_2O}$ METERS / SEC	2.61727E 03	2.64617E 03	2.69199E 03	2.71393E 03	2.73482E 03	2.79402E 03
$\gamma''_{CO_2}$ METERS / SEC	1.67651E 03	1.90593E 03	1.97472E 03	2.00465E 03	2.03307E 03	2.09077E 03
$\gamma''_{CO}$ METERS / SEC	1.67074E 03	1.90012E 03	1.98149E 03	2.00852E 03	2.03701E 03	2.10173E 03
$u''$ METERS / SEC	1.67673E 03	1.90010E 03	1.98155E 03	2.00850E 03	2.03707E 03	2.10170E 03
$M''_{(H_2)}$	9.31354E -01	9.35363E -01	9.47206E -01	9.50164E -01	9.56505E -01	9.66267E -01
$M''_{(O_2)}$	1.00122E 00	1.00110E 00	1.00366E 00	1.00196E 00	1.00197E 00	1.00146E 00
$M''_{(H_2O)}$	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00
$P_{NS}''$	2.95049E 01	3.03147E 01	3.22113E 01	3.30215E 01	3.38175E 01	3.56679E 01
$P_{NS}''$	4.29016E 00	4.31602E 00	4.34055E 00	4.36225E 00	4.37515E 00	4.40074E 00
$T_{NS}$ DEG K	2.09451E 03	2.10011E 03	2.22221E 03	2.27095E 03	2.31083E 03	2.42612E 03
$M_{NS}$	4.41740E -01	4.40094E -01	4.39057E -01	4.38336E -01	4.37666E -01	4.36767E -01
$P_{(NS)}$ ATMOS	6.12630E 01	1.26640E 02	6.78619E 02	1.39680E 03	2.87163E 03	1.52159E 04

TABLE 6. CALCULATED DETONATION PARAMETERS FOR  $H_2 - O_2 - A$  MIXTURES  
 $(2H_2 + O_2) + 1/3 A$ 

66 2/3 % $H_2$ IN THE BASIC (STOICHIOMETRIC) $H_2 - O_2$ MIXTURE (BY VOLUME) 10% A							
INITIAL TEMPERATURE 300° K							
$n^* = 3 1/3$ GM MOLES $m^* = 14.0000$ $\gamma^* = 3.30220$ $c_h = 400.000$ METERS PER SEC							
DETONATION PARAMETERS	INITIAL PRESSURE, ATMOSPHERES						
	0.5	1	5	10	20	100	1000
$T^*$ DEG K	3.56120E-02	3.62670E-02	3.70010E-02	3.76400E-02	3.80940E-02	3.84270E-02	3.89650E-02
$P^*/P^0$	1.01440E-01	1.02037E-01	1.02700E-01	1.03200E-01	1.03653E-01	1.04060E-01	1.04427E-01
$P^*/P^0$	0.54530E-01	0.55751E-01	0.56810E-01	0.57751E-01	0.58590E-01	0.59327E-01	0.59957E-01
$P^*$ CM/CM <sup>3</sup>	3.00000E-04	0.01302E-04	3.00000E-03	0.01302E-03	1.30270E-02	0.01302E-02	0.01302E-01
$m^*/m^0$	1.10022E-00	1.10040E-00	1.21766E-00	1.23007E-00	1.24321E-00	1.27040E-00	1.32210E-00
$D$ METERS / SEC	2.51977E-03	2.53040E-03	2.62632E-03	2.64757E-03	2.70077E-03	2.77603E-03	2.86362E-03
$M^*$	5.15000E-00	5.22610E-00	5.39120E-00	5.46120E-00	5.50720E-00	5.67910E-00	5.95000E-00
$P^*$ ATMOS	1.57200E-01	1.62000E-01	1.70700E-01	1.74000E-01	1.76000E-01	1.76000E-01	1.76000E-01
$n^*$ GM MOLES	2.00000E-00	2.70000E-00	2.70000E-00	2.70000E-00	2.70000E-00	2.70000E-00	2.70000E-00
$X_A$	1.10022E-01	1.10040E-01	1.21766E-01	1.23007E-01	1.24321E-01	1.27040E-01	1.32210E-01
$X_H$	7.57700E-02	6.75000E-02	5.17700E-02	5.10000E-02	5.00000E-02	5.00000E-02	5.00000E-02
$X_O$	1.00000E-01	1.01600E-01	1.20000E-01	1.25000E-01	1.25000E-01	1.00000E-01	0.24000E-02
$X_{H_2O}$	0.00000E-01	0.00000E-01	0.12000E-01	0.27000E-01	0.50000E-01	0.00000E-01	0.00000E-01
$X_{CO}$	0.00000E-02	0.17770E-02	0.00000E-02	0.00000E-02	1.00000E-02	1.00000E-02	0.00000E-02
$X_{CO_2}$	0.00000E-02	0.00000E-02	0.00000E-02	0.00000E-02	0.00000E-02	0.00000E-02	0.00000E-02
$X_{H_2O}$	0.00000E-00	0.00000E-00	0.00000E-00	0.00000E-00	0.00000E-00	0.00000E-00	0.00000E-00
$X_{CO}$	1.15000E-01	1.16000E-01	1.16000E-01	1.15700E-01	1.15600E-01	1.00000E-01	0.32000E-02
$Y_{H_2O}$	1.20000E-00	1.20000E-00	1.22000E-00	1.22000E-00	1.21000E-00	1.21000E-00	1.19000E-00
$Y_{H_2}$	1.21000E-00	1.21000E-00	1.21000E-00	1.21000E-00	1.21000E-00	1.20700E-00	1.20700E-00
$Y_{H_2O}$	1.13150E-00	1.13070E-00	1.14530E-00	1.15000E-00	1.15000E-00	1.16000E-00	1.17310E-00
$c_{H_2O}$ METERS / SEC	1.03671E-03	1.03310E-03	1.09110E-03	1.07000E-03	1.02000E-03	1.00000E-03	1.00000E-03
$c_{H_2}$ METERS / SEC	1.07100E-03	1.06000E-03	1.00000E-03	1.00000E-03	1.00000E-03	1.00000E-03	1.00000E-03
$c_{H_2O}$ METERS / SEC	1.07100E-03	1.06000E-03	1.00000E-03	1.00000E-03	1.00000E-03	1.00000E-03	1.00000E-03
$u^*$ METERS / SEC	1.07100E-03	1.06000E-03	1.00000E-03	1.00000E-03	1.00000E-03	1.00000E-03	1.00000E-03
$M_{H_2O}$	0.55750E-01	0.59300E-01	0.66000E-01	0.70311E-01	0.73000E-01	0.80700E-01	0.90000E-01
$M_{H_2}$	1.00100E-00	1.00150E-00	1.00000E-00	1.00150E-00	1.00100E-00	1.00150E-00	1.00150E-00
$M_{H_2O}$	1.00000E-00	1.00000E-00	1.00000E-00	1.00000E-00	1.00000E-00	1.00000E-00	1.00000E-00
$P_{H_2O}$	3.00000E-01	3.10000E-01	3.39100E-01	3.40100E-01	3.50100E-01	3.70000E-01	4.00000E-01
$P_{H_2}$	0.00100E-00	0.02210E-00	0.00000E-00	0.00000E-00	0.00170E-00	0.03710E-00	0.07000E-00
$T_{H_2O}$ DEG K	1.00000E-03	1.00100E-03	2.00000E-03	2.00000E-03	2.10000E-03	2.20000E-03	2.30000E-03
$M_{H_2}$	0.10010E-01	0.17300E-01	0.15370E-01	0.14500E-01	0.13000E-01	0.12550E-01	0.10000E-01
$P_{H_2O}$ ATMOS	1.00100E-01	1.01900E-01	0.17510E-01	1.00500E-01	0.07030E-01	1.00000E-01	1.00000E-01

TABLE 7. CALCULATED DETONATION PARAMETERS FOR  $H_2 - O_2 - A$  MIXTURES  
 $(2H_2 + O_2) + A$   
 66.2/3 %  $H_2$  IN THE BASIC (STOICHIOMETRIC)  $H_2 - O_2$  MIXTURE (BY VOLUME) 25 % A  
 INITIAL TEMPERATURE 300° K  
 $n' = 4$  GM MOLES  $m' = 16.99480$   $\gamma' = 3.24350$   $a_0' = 435.7337$  METERS PER SEC

DETONATION PARAMETERS	INITIAL PRESSURE, ATMOSPHERES						
	0.5	1	5	10	20	100	1000
$T''$ DEG K	3.43193E 03	3.54027E 03	3.83345E 03	3.96162E 03	4.09170E 03	4.39397E 03	4.79596E 03
$\rho'' / \rho'$	1.01145E 01	1.05723E 01	1.06202E 01	2.00073E 01	2.05441E 01	2.15649E 01	2.27970E 01
$\rho'' / \rho''$	5.44094E -01	5.47439E -01	5.49420E -01	5.50487E -01	5.51257E -01	5.53293E -01	5.55490E -01
$\rho''$ GM / CM <sup>3</sup>	3.05003E -04	7.71606E -04	3.05003E -03	7.71606E -03	1.54321E -02	7.71606E -02	7.71606E -01
$m'' / m'$	1.15493E 00	1.16331E 00	1.18446E 00	1.19422E 00	1.20432E 00	1.22056E 00	1.26236E 00
$D$ METERS / SEC	2.22699E 03	2.25015E 03	2.33045E 03	2.36145E 03	2.39159E 03	2.45776E 03	2.53771E 03
$M'$	5.11089E 00	5.18241E 00	5.34879E 00	5.41967E 00	5.48844E 00	5.64051E 00	5.82400E 00
$P'$ ATMOS	1.56495E 01	3.20990E 01	1.69462E 02	3.44735E 02	7.09072E 02	3.71557E 03	3.92407E 04
$n''$ GM MOLES	3.54340E 00	3.43947E 00	3.37707E 00	3.34967E 00	3.32130E 00	3.25585E 00	3.16846E 00
$X_A$	2.00733E -01	2.90027E -01	2.96114E -01	2.96554E -01	3.01000E -01	3.07139E -01	3.15591E -01
$X_H$	5.61906E -02	5.06336E -02	3.81073E -02	3.36132E -02	2.81005E -02	1.82946E -02	8.20767E -03
$X_{H_2O}$	1.13095E -01	1.10740E -01	1.03424E -01	9.93016E -02	9.47600E -02	8.10193E -02	6.81297E -02
$X_{CO}$	3.91770E -01	4.00015E -01	4.25433E -01	4.37645E -01	4.50042E -01	4.84700E -01	5.37295E -01
$X_{CO_2}$	2.57135E -02	2.35443E -02	1.04123E -02	1.61975E -02	1.60277E -02	9.37040E -03	4.34910E -03
$X_{H_2}$	3.54834E -02	3.30540E -02	2.90734E -02	2.80572E -02	2.61802E -02	2.16305E -02	1.51049E -02
$X_{H_2O}$	3.40910E -00	5.31094E -00	1.45045E -07	2.10319E -07	3.23207E -07	7.35457E -07	2.01329E -06
$X_{OH}$	8.90121E -02	8.95640E -02	8.86355E -02	8.71512E -02	8.49337E -02	7.68653E -02	5.93291E -02
$Y_{H_2O}$	1.27030E 00	1.24474E 00	1.25430E 00	1.25467E 00	1.25107E 00	1.24305E 00	1.23310E 00
$Y_{CO_2}$	1.20049E 00	1.20213E 00	1.20550E 00	1.20700E 00	1.20853E 00	1.21152E 00	1.21440E 00
$Y_{CO}$	1.13099E 00	1.14451E 00	1.15821E 00	1.16366E 00	1.16845E 00	1.18112E 00	1.19485E 00
$q''_{H_2O}$ METERS / SEC	1.20551E 03	1.30054E 03	1.33519E 03	1.34982E 03	1.36400E 03	1.39506E 03	1.43204E 03
$q''_{CO_2}$ METERS / SEC	1.21620E 03	1.23695E 03	1.27001E 03	1.29767E 03	1.31620E 03	1.35743E 03	1.40782E 03
$q''_{H_2}$ METERS / SEC	1.21773E 03	1.23620E 03	1.20099E 03	1.29995E 03	1.31030E 03	1.35904E 03	1.40947E 03
$u''$ METERS / SEC	1.21777E 03	1.23624E 03	1.20103E 03	1.29990E 03	1.31042E 03	1.35990E 03	1.40972E 03
$M''$ (g)	9.47304E -01	9.5053E -01	9.59434E -01	9.63079E -01	9.66520E -01	9.74800E -01	9.84590E -01
$M''$ (g)	1.00122E 00	1.00104E 00	1.00174E 00	1.00170E 00	1.00163E 00	1.00102E 00	1.00134E 00
$M''$ (g)	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00
$P_{NS}$ (g)	3.04995E 01	3.15490E 01	3.34614E 01	3.45412E 01	3.54332E 01	3.74314E 01	3.99105E 01
$P_{NS}$ (g)	4.68244E 00	4.70153E 00	4.74311E 00	4.75983E 00	4.77549E 00	4.80880E 00	4.84595E 00
$T_{NS}$ DEG K	1.94401E 03	2.01444E 03	2.12780E 03	2.17704E 03	2.22505E 03	2.33510E 03	2.47125E 03
$M_{NS}$	4.26271E -01	4.25379E -01	4.23435E -01	4.22441E -01	4.21931E -01	4.20410E -01	4.18761E -01
$P_{NS}$ ATMOS	6.95340E 01	1.43725E 02	7.74100E 02	1.59651E 03	3.28845E 03	1.75191E 04	1.00597E 05

TABLE 8. CALCULATED DETONATION PARAMETERS FOR  $H_2 - O_2 - A$  MIXTURES  
 $(2H_2 + O_2) + 1.8 A$   
 66.2/3 %  $H_2$  IN THE BASIC (STOICHIOMETRIC)  $H_2 - O_2$  MIXTURE (BY VOLUME) 37.5 % A  
 INITIAL TEMPERATURE 300° K  
 $n' = 4.8$  GM. MOLES  $m' = 22.4857$   $\gamma' = 1.1928$   $c_s = 484.669$  METERS PER SEC

DETONATION PARAMETERS	INITIAL PRESSURE, ATMOSPHERES						
	0.1	1	5	10	20	100	1000
$T^*$ DEG K	3.35745E 03	3.44424E 03	3.72971E 03	3.86430E 03	3.96345E 03	4.23241E 03	4.57939E 03
$P^* / P'$	1.79732E 01	1.84250E 01	1.94421E 01	1.98001E 01	2.02906E 01	2.12404E 01	2.23703E 01
$\rho^* / \rho'$	5.40773E -01	5.45407E -01	5.52139E -01	5.53214E -01	5.57706E -01	5.67310E -01	5.80037E -01
$\rho^*$ GM / CM <sup>3</sup>	0.54725E -04	0.13050E -04	0.54725E -03	0.13050E -03	1.00600E -02	0.13050E -02	0.13050E -01
$m^* / m'$	1.13463E 00	1.14139E 00	1.19010E 00	1.16576E 00	1.17304E 00	1.19100E 00	1.21625E 00
$D$ METERS / SEC	2.84200E 03	2.87127E 03	2.11739E 03	2.16514E 03	2.19207E 03	2.25210E 03	2.32305E 03
$M^*$	5.85557E 00	5.12603E 00	1.20943E 00	5.34834E 00	5.42590E 00	5.57344E 00	5.75110E 00
$P^*$ ATMOS	1.54641E 01	3.17174E 01	1.67004E 02	3.61279E 02	6.95549E 02	3.63104E 03	3.81104E 04
$n$ GM MOLES	4.23045E 00	4.20537E 00	4.14457E 00	4.11749E 00	4.09011E 00	4.07537E 00	3.99424E 00
$X_{H_2}$	4.25408E -01	4.28007E -01	4.34303E -01	4.37159E -01	4.40064E -01	4.44074E -01	4.54073E -01
$X_{H_2O}$	4.14442E -02	3.72000E -02	2.73540E -02	2.34194E -02	1.97375E -02	1.24140E -02	5.21054E -03
$X_{H_2O}$	9.81978E -02	8.59122E -02	7.96399E -02	7.53937E -02	7.13409E -02	6.49473E -02	5.27895E -02
$X_{H_2O}$	3.29713E -01	3.59799E -01	3.54449E -01	3.64244E -01	3.74545E -01	4.02275E -01	4.40574E -01
$X_{H_2O}$	1.88019E -02	1.70917E -02	1.34410E -02	1.13704E -02	9.44283E -03	6.76443E -03	2.74932E -03
$X_{H_2O}$	2.80230E -02	2.68011E -02	2.32210E -02	2.17049E -02	2.01124E -02	1.83204E -02	1.16790E -02
$X_{H_2O}$	2.13313E -02	2.31444E -02	9.00794E -02	1.30371E -07	1.00401E -07	4.13212E -07	1.01904E -06
$X_{H_2O}$	4.80423E -02	5.61051E -02	6.63594E -02	6.47303E -02	6.25319E -02	5.53614E -02	4.12634E -02
$Y_{H_2}$	1.36237E 00	1.29929E 00	1.20054E 00	1.20743E 00	1.20400E 00	1.27649E 00	1.26772E 00
$Y_{H_2O}$	1.19442E 00	1.19759E 00	1.20340E 00	1.20032E 00	1.21204E 00	1.22039E 00	1.23155E 00
$Y_{H_2O}$	1.14041E 00	1.15312E 00	1.14943E 00	1.17593E 00	1.18043E 00	1.19943E 00	1.21999E 00
$C_{H_2}$ METERS / SEC	1.19373E 03	1.20774E 03	1.23904E 03	1.25329E 03	1.26634E 03	1.29401E 03	1.32054E 03
$C_{H_2O}$ METERS / SEC	1.12093E 03	1.13739E 03	1.17870E 03	1.19447E 03	1.21392E 03	1.25204E 03	1.30004E 03
$C_{H_2O}$ METERS / SEC	1.12107E 03	1.13797E 03	1.18009E 03	1.19779E 03	1.21632E 03	1.25514E 03	1.30330E 03
$u^*$ METERS / SEC	1.12111E 03	1.13804E 03	1.18013E 03	1.19783E 03	1.21635E 03	1.25516E 03	1.30333E 03
$M_{H_2}^*$	9.39161E -01	9.42244E -01	9.51834E -01	9.55740E -01	9.60523E -01	9.69300E -01	9.81024E -01
$M_{H_2O}^*$	1.00093E 00	1.00034E 00	1.00114E 00	1.00112E 00	1.00200E 00	1.00105E 00	1.00190E 00
$M_{H_2O}^*$	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00
$P_{H_2} / P'$	3.62644E 01	3.11004E 01	5.31277E 01	3.40012E 01	3.60400E 01	3.60041E 01	3.91973E 01
$P_{H_2O} / P'$	4.49502E 00	4.51135E 00	4.54900E 00	4.56514E 00	4.57974E 00	4.61000E 00	4.64394E 00
$T_{H_2}$ DEG K	2.61919E 03	2.60010E 03	2.10434E 03	2.23440E 03	2.30410E 03	2.39503E 03	2.53919E 03
$M_{H_2}$	6.35444E -01	4.35754E -01	4.30043E -01	4.30007E -01	4.29574E -01	4.27092E -01	4.24044E -01
$P_{H_2O}$ ATMOS	6.57144E 01	1.35794E 02	7.30072E 02	1.50400E 03	3.16230E 03	1.65040E 04	1.77307E 05



TABLE 9. CALCULATED DETONATION PARAMETERS FOR  $H_2 - O_2 - A$  MIXTURES

$(2H_2 + O_2) + 3A$ 66 2/3 % $H_2$ IN THE BASIC (STOICHIOMETRIC) $H_2 - O_2$ MIXTURE (BY VOLUME) 50 % A INITIAL TEMPERATURE 300° K $n' = 6$ G/M MOLES $m' = 25.9773$ $\gamma' = 2.99567$ $a_n' = 379.6566$ METERS PER SEC									
DETONATION PARAMETERS	INITIAL PRESSURE, ATMOSPHERES								
	0.5	1	2	10	20	100	1000		
$T''$ DEG K	3.25704E 03	3.35492E 03	3.58710E 03	3.68920E 03	3.78958E 03	4.01387E 03	4.28798E 03		
$P'' / P'$	1.74344E 01	1.80422E 01	1.89309E 01	1.93512E 01	1.97281E 01	2.15641E 01	2.14505E 01		
$\rho'' / \rho'$	5.52239E-01	5.53404E-01	5.57613E-01	5.58266E-01	5.59742E-01	5.63018E-01	5.68193E-01		
$P''$ GM / CM <sup>3</sup>	5.27647E-04	1.05529E-03	5.27647E-03	1.05529E-02	2.11059E-02	1.05529E-01	1.05529E 00		
$m'' / m'$	1.11405E 00	1.12002E 00	1.13273E 00	1.13824E 00	1.14388E 00	1.15662E 00	1.17273E 00		
$D$ METERS / SEC	1.88873E 03	1.91623E 03	1.97282E 03	1.99735E 03	2.02111E 03	2.07246E 03	2.13253E 03		
$P''_I$ ATMOS	4.97483E 00	5.04201E 00	5.19634E 00	5.26088E 00	5.32333E 00	5.55870E 00	5.61699E 00		
$n''$ G/M MOLES	1.50409E 01	3.07953E 01	1.60782E 02	3.28706E 02	6.69144E 02	3.47168E 03	5.99021E 04		
$x''_A$	5.57426E-01	5.60012E-01	5.66366E-01	5.69138E-01	5.71962E-01	5.78309E-01	5.86366E-01		
$x''_H$	2.77741E-02	2.46526E-02	1.72879E-02	1.45439E-02	1.20238E-02	7.19645E-03	2.05566E-03		
$x''_{H_2O}$	6.39704E-02	6.18148E-02	5.55199E-02	5.23770E-02	4.89493E-02	4.01896E-02	2.71587E-02		
$x''_{CO}$	2.60772E-01	2.75513E-01	2.90622E-01	2.97966E-01	3.05560E-01	3.23979E-01	3.49767E-01		
$x''_{CO_2}$	1.22799E-02	1.18131E-02	8.06978E-03	6.88922E-03	5.76879E-03	3.56767E-03	1.44858E-03		
$x''_{O_2}$	2.07872E-02	1.96266E-02	1.67519E-02	1.54050E-02	1.42094E-02	1.12326E-02	7.28853E-03		
$x''_{H_2}$	1.15377E-08	1.75970E-08	4.42044E-08	6.42382E-08	9.16082E-08	1.86356E-07	6.13979E-07		
$x''_{OH}$	4.79762E-02	4.75737E-02	4.51834E-02	4.35778E-02	4.15468E-02	3.55646E-02	2.51172E-02		
$Y''_{H_2O}$	1.34130E 00	1.33809E 00	1.33676E 00	1.32770E 00	1.32471E 00	1.31831E 00	1.31081E 00		
$Y''_{CO}$	1.19424E 00	1.19912E 00	1.21168E 00	1.21762E 00	1.22374E 00	1.23853E 00	1.25893E 00		
$Y''_{CO_2}$	1.16340E 00	1.17040E 00	1.19388E 00	1.19899E 00	1.20785E 00	1.22571E 00	1.25451E 00		
$u''_{H_2O}$ METERS / SEC	1.11994E 03	1.13265E 03	1.16142E 03	1.17360E 03	1.18520E 03	1.21010E 03	1.23858E 03		
$u''_{CO}$ METERS / SEC	1.04179E 03	1.05812E 03	1.09632E 03	1.11293E 03	1.12916E 03	1.16518E 03	1.20896E 03		
$u''_{CO_2}$ METERS / SEC	1.04303E 03	1.05936E 03	1.10007E 03	1.11500E 03	1.13134E 03	1.16683E 03	1.21169E 03		
$u''$ METERS / SEC	1.04306E 03	1.05938E 03	1.10011E 03	1.11511E 03	1.13138E 03	1.16686E 03	1.21172E 03		
$M''_{H_2O}$	9.31354E-01	9.35304E-01	9.47205E-01	9.50165E-01	9.54588E-01	9.64266E-01	9.78316E-01		
$M''_{CO}$	1.00122E 00	1.00118E 00	1.00346E 00	1.00196E 00	1.00197E 00	1.00144E 00	1.00228E 00		
$M''_{CO_2}$	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00		
$P''_{NS} / P'$	2.95069E 01	3.03147E 01	3.22113E 01	3.30215E 01	3.38175E 01	3.55679E 01	3.76713E 01		
$P''_{NS} / P''$	4.29816E 00	4.31462E 00	4.34855E 00	4.36225E 00	4.37515E 00	4.40174E 00	4.43081E 00		
$T''_{NS}$ DEG K	2.05951E 03	2.10811E 03	2.22221E 03	2.27095E 03	2.31883E 03	2.42412E 03	2.55046E 03		
$M''_{NS}$	4.41748E-01	4.40896E-01	4.39057E-01	4.38334E-01	4.37636E-01	4.36269E-01	4.34767E-01		
$P''_{(NS)}$ ATMOS	6.12636E 01	1.26444E 02	6.78619E 02	1.39686E 03	2.87163E 03	1.52159E 04	1.62489E 05		

TABLE 10. CALCULATED DETONATION PARAMETERS FOR  $H_2 - O_2 - CO_2$  MIXTURES

$2H_2 + O_2 + 10 CO_2$ 66.25 % $H_2$ IN THE BASIC (STOICHIOMETRIC) $H_2 - O_2$ MIXTURE (BY VOLUME) 4 % $CO_2$ INITIAL TEMPERATURE 300° K $n' = 3.18$ G/M MOLES $m' = 13.2970$ $\gamma' = 3.93072$ $a_0 = 51.7018$ METERS PER SEC								
DETONATION PARAMETERS		INITIAL PRESSURE, ATMOSPHERES						
		0.5	1	2	5	10	20	100
$T^*$ DEG K		3.46105E-03	3.57273E-03	3.67072E-03	3.80154E-03	3.93457E-03	4.04505E-03	4.04704E-02
$P^*/P'$		1.76654E-01	1.80762E-01	1.89570E-01	1.96630E-01	1.98400E-01	2.07579E-01	2.10062E-01
$\rho^*/\rho'$		3.33019E-01	3.36377E-01	3.39323E-01	3.46100E-01	3.46400E-01	3.57881E-01	3.58063E-01
$P^*$ G/M CM <sup>2</sup>		2.69950E-04	3.39917E-04	2.69950E-03	3.39917E-03	1.07003E-02	3.39917E-02	3.39917E-01
$u^*$ / m'		1.20110E-00	1.21253E-00	1.29127E-00	1.35477E-00	1.36000E-00	1.36000E-00	1.36759E-00
$D$ METERS / SEC		2.61867E-03	2.66817E-03	2.73000E-03	2.78200E-03	2.77200E-03	2.86300E-03	2.95000E-03
$M^*$		3.11710E-00	3.16370E-00	3.33603E-00	3.40000E-00	3.40210E-00	3.59673E-00	3.75300E-00
$P^*$ ATMOS		1.53020E-01	1.59470E-01	1.65630E-01	1.70000E-01	1.70000E-01	1.70000E-01	1.70000E-01
$n^*$ G/M MOLES		2.66140E-00	2.57720E-00	2.51700E-00	2.40000E-00	2.40000E-00	2.30000E-00	2.31000E-00
$x_{CO_2}^*$		3.30000E-11	1.35627E-10	3.93407E-10	9.22040E-10	1.07000E-09	3.99000E-09	3.00730E-09
$x_{H_2}^*$		0.	0.	0.	0.	0.	0.	0.
$x_{O_2}^*$		2.67100E-17	8.73000E-17	1.30000E-16	3.20000E-16	1.30000E-16	1.30000E-16	1.30000E-16
$x_{H_2O}^*$		1.00000E-21	3.61000E-21	2.50000E-20	1.30000E-20	3.01000E-20	1.30000E-20	3.01000E-20
$x_{CO}^*$		1.30000E-11	3.30000E-11	2.60000E-10	3.71000E-10	1.00000E-09	3.00000E-09	1.77000E-09
$x_{H_2}^*$		2.60000E-10	3.60000E-10	3.30000E-09	6.07000E-09	1.30000E-08	3.20000E-08	3.70000E-07
$x_{O_2}^*$		9.90000E-12	2.60700E-11	2.60000E-10	6.30000E-10	1.00000E-09	1.00000E-09	1.00000E-07
$x_{H_2O}^*$		2.00000E-12	3.20700E-12	7.50000E-11	2.70000E-10	6.00000E-10	3.00000E-09	1.00000E-07
$x_{CO}^*$		2.90000E-10	9.23167E-10	1.60700E-10	3.30000E-10	1.00000E-10	2.11000E-11	6.00000E-10
$x_{H_2}^*$		4.27000E-10	3.51317E-10	1.60100E-10	7.00000E-10	3.00000E-10	1.00000E-11	1.00000E-11
$x_{O_2}^*$		3.00000E-06	3.60000E-06	3.60000E-06	3.70000E-06	3.70000E-06	1.00000E-06	4.30000E-06
$x_{H_2O}^*$		3.20000E-02	3.22000E-02	3.10000E-02	3.10000E-02	3.10000E-02	2.00117E-02	2.00000E-02
$x_{CO}^*$		1.50010E-02	1.62710E-02	1.77000E-02	1.80000E-02	1.80000E-02	2.00000E-02	2.00000E-02
$x_{H_2}^*$		6.72010E-02	6.05700E-02	6.50770E-02	3.90000E-02	3.00000E-02	2.90000E-02	9.01700E-03
$x_{O_2}^*$		1.37000E-01	1.30000E-01	1.30000E-01	1.10000E-01	1.10000E-01	9.70000E-02	7.10000E-02
$x_{H_2O}^*$		3.30000E-01	3.00000E-01	3.00000E-01	6.00000E-01	6.20000E-01	6.70000E-01	7.60000E-01
$x_{CO}^*$		3.60000E-02	3.10000E-02	2.50000E-02	2.20000E-02	1.90000E-02	1.30000E-02	6.50000E-03
$x_{H_2}^*$		3.30000E-02	3.17100E-02	6.65510E-02	6.61000E-02	6.61000E-02	3.00000E-02	2.61200E-02
$x_{O_2}^*$		6.50200E-00	1.00000E-07	2.90000E-07	6.60000E-07	6.00000E-07	1.00000E-06	6.70000E-06
$x_{H_2O}^*$		1.22167E-01	1.23210E-01	1.23000E-01	1.21000E-01	1.10000E-01	1.00000E-01	6.90000E-02
$M^*$		1.59000E-01	1.61150E-01	1.60720E-01	1.60700E-01	1.60600E-01	1.73100E-01	1.79700E-01
$\gamma^*$		1.21550E-00	1.21200E-00	1.20300E-00	1.20000E-00	1.19700E-00	1.10910E-00	1.17000E-00
$\gamma^*$		1.10930E-00	1.10900E-00	1.10000E-00	1.10000E-00	1.10000E-00	1.10000E-00	1.11200E-00
$\gamma^*$		1.12040E-00	1.12040E-00	1.12000E-00	1.10100E-00	1.10100E-00	1.10100E-00	1.10700E-00
$\gamma^*$		1.40000E-03	1.40000E-03	1.50000E-03	1.50000E-03	1.50000E-03	1.00000E-03	1.00000E-03
$\gamma^*$		1.36650E-03	1.30540E-03	1.40000E-03	1.40000E-03	1.40000E-03	1.50000E-03	1.50000E-03
$\gamma^*$		1.42300E-03	1.40000E-03	1.40000E-03	1.50000E-03	1.50000E-03	1.50000E-03	1.61000E-03
$\gamma^*$		1.40000E-03	1.40000E-03	1.40000E-03	1.50000E-03	1.50000E-03	1.50000E-03	1.61000E-03
$M^*$		9.61000E-01	9.60000E-01	9.71000E-01	9.73230E-01	9.70100E-01	9.00000E-01	9.00000E-01
$M^*$		1.00000E-00	1.00000E-00	1.00170E-00	1.00000E-00	1.00100E-00	1.00000E-00	1.00000E-00
$M^*$		1.00000E-00	1.00000E-00	1.00000E-00	1.00000E-00	1.00000E-00	1.00000E-00	1.00000E-00
$P^*$		3.03000E-01	3.11300E-01	3.20000E-01	3.30000E-01	3.40000E-01	3.60000E-01	3.80000E-01
$P^*$		3.07000E-00	3.10000E-00	3.10000E-00	3.10000E-00	3.10000E-00	3.21000E-00	3.30000E-00
$T^*$ DEG K		1.79190E-03	1.83100E-03	1.92000E-03	1.96300E-03	2.00200E-03	2.00000E-03	2.10200E-03
$M^*$		4.12170E-01	4.11300E-01	4.09100E-01	4.00000E-01	4.07000E-01	4.00000E-01	4.00000E-01
$P^*$ ATMOS		1.45100E-01	1.53700E-02	8.23000E-02	1.60000E-03	3.40170E-03	1.00000E-00	1.00000E-00

TABLE 11. CALCULATED DETONATION PARAMETERS FOR  $H_2 - O_2 - CO_2$  MIXTURES  
 $(24 + O_2) + 1/3 CO_2$   
 66.25 %  $H_2$  IN THE BASIC (STOICHIOMETRIC)  $H_2 - O_2$  MIXTURE (BY VOLUME) 10 %  $CO_2$   
 INITIAL TEMPERATURE 3000 K  
 $n' = 3 \text{ 1/3}$  G.M. MOLES  $m' = 15.2074$   $\gamma' = 3.5000$   $a_0' = 476.7730$  METERS PER SEC

DETONATION PARAMETERS	INITIAL PRESSURE, ATMOSPHERES						
	0.5	1	5	10	20	100	1000
$T'$ DEG K	3.33045E 03	3.44341E 03	3.69607E 03	3.81012E 03	3.92204E 03	4.10620E 03	4.53610E 03
$P'/P'$	1.69820E 01	1.73742E 01	1.81904E 01	1.8947E 01	1.96431E 01	1.97009E 01	2.07137E 01
$\rho'/\rho'$	5.44170E -01	5.44003E -01	5.44077E -01	5.44099E -01	5.44200E -01	5.44273E -01	5.47359E -01
$\rho'$ GM/CM <sup>3</sup>	3.00950E -04	6.17916E -04	3.00950E -03	6.17916E -03	1.23583E -02	6.17916E -02	6.17916E -01
$m'/m'$	1.20424E 00	1.21440E 00	1.24000E 00	1.25163E 00	1.26341E 00	1.29230E 00	1.33303E 00
$D$ METERS / SEC	2.39770E 03	2.42644E 03	2.49240E 03	2.52017E 03	2.54662E 03	2.60423E 03	2.67750E 03
$M'$	5.00950E 00	5.00950E 00	5.22022E 00	5.20807E 00	5.36137E 00	5.46219E 00	5.60539E 00
$P_1'$ ATMOS	1.66044E 01	3.00993E 01	1.57070E 02	3.23432E 02	6.56919E 02	3.44053E 03	6.60461E 04
$n'$ G.M. MOLES	2.76794E 09	2.76404E 09	2.40010E 09	2.46320E 09	2.43794E 09	2.57937E 09	2.50957E 09
$X_{H_2}$	6.12974E -11	1.00091E -10	3.63074E -10	5.70404E -10	8.65342E -10	1.90007E -09	3.50303E -09
$X_{O_2}$	0.	0.	0.	0.	0.	0.	0.
$X_{CO_2}$	2.05322E -17	9.36400E -17	1.23993E -15	3.40757E -15	9.11120E -15	6.90104E -14	4.20607E -13
$X_{H_2O}$	2.21830E -21	1.12960E -20	4.11910E -19	1.77467E -18	7.02000E -18	1.37095E -16	4.51009E -15
$X_{CO}$	1.22639E -11	3.62572E -11	1.60716E -10	3.11970E -10	5.73431E -10	2.03104E -09	7.52267E -09
$X_{H_2O_2}$	2.22039E -10	4.70944E -10	2.57100E -09	5.09673E -09	9.00904E -09	3.66347E -08	1.90304E -07
$X_{H_2O_2}$	9.16099E -12	2.22563E -11	1.95256E -10	6.66699E -10	1.06341E -09	6.78366E -09	6.31973E -08
$X_{H_2O_2}$	2.30891E -12	6.03160E -12	6.51044E -11	1.76797E -10	6.65951E -10	6.04050E -09	6.04765E -08
$X_{H_2O_2}$	4.66200E -13	1.50163E -14	2.36670E -13	6.94461E -13	2.02001E -12	2.12643E -11	3.76659E -10
$X_{H_2O_2}$	6.60009E -19	3.50907E -18	1.65903E -16	8.20771E -16	3.91910E -15	1.27555E -13	1.12046E -11
$X_{H_2O_2}$	6.60633E -04	1.35913E -03	3.65169E -05	5.67926E -05	8.06609E -05	1.05491E -04	4.97300E -04
$X_{H_2O_2}$	7.04946E -02	7.00605E -02	6.75354E -02	6.50342E -02	6.42017E -02	5.01317E -02	4.50622E -02
$X_{H_2O_2}$	6.99232E -02	5.13595E -02	5.64275E -02	5.92535E -02	6.20793E -02	7.09119E -02	8.69627E -02
$X_{H_2O_2}$	4.36194E -02	3.05154E -02	2.76736E -02	2.35134E -02	1.96160E -02	1.21049E -02	5.20639E -03
$X_{H_2O_2}$	1.00320E -01	9.66034E -02	8.64105E -02	8.15169E -02	7.60424E -02	6.26099E -02	4.51164E -02
$X_{H_2O_2}$	5.60090E -01	5.61255E -01	5.93542E -01	6.00607E -01	6.24701E -01	6.06024E -01	7.21370E -01
$X_{H_2O_2}$	2.49540E -02	2.80733E -02	1.83041E -02	1.59029E -02	1.37633E -02	9.11357E -03	4.23950E -03
$X_{H_2O_2}$	5.74270E -02	5.52590E -02	4.96523E -02	4.70767E -02	4.46650E -02	3.70070E -02	2.77943E -02
$X_{H_2O_2}$	5.00044E -00	9.20123E -00	2.55050E -07	3.04500E -07	5.75443E -07	1.36151E -06	3.72290E -06
$X_{H_2O_2}$	1.03053E -01	1.03074E -01	1.00450E -01	9.81621E -02	9.49901E -02	8.69376E -02	6.49309E -02
$X_{H_2O_2}$	1.03177E 01	1.04710E 01	1.00612E 01	1.90302E 01	1.92203E 01	1.90560E 01	2.02763E 01
$Y_{H_2}$	1.20003E 00	1.20505E 00	1.19794E 00	1.19494E 00	1.19199E 00	1.10534E 00	1.17694E 00
$Y_{H_2O}$	1.06552E 00	1.06041E 00	1.06946E 00	1.07120E 00	1.07301E 00	1.07042E 00	1.06907E 00
$Y_{H_2O_2}$	1.12352E 00	1.12633E 00	1.13691E 00	1.13650E 00	1.14044E 00	1.14124E 00	1.15000E 00
$u_{H_2}$ METERS / SEC	1.35304E 03	1.36640E 03	1.39726E 03	1.41013E 03	1.42220E 03	1.44077E 03	1.47922E 03
$u_{H_2O}$ METERS / SEC	1.23000E 03	1.25011E 03	1.29267E 03	1.30807E 03	1.32452E 03	1.36040E 03	1.40500E 03
$u_{H_2O_2}$ METERS / SEC	1.30404E 03	1.32011E 03	1.36119E 03	1.37525E 03	1.39117E 03	1.42150E 03	1.46202E 03
$u'$ METERS / SEC	1.30490E 03	1.32015E 03	1.36129E 03	1.37529E 03	1.39121E 03	1.42162E 03	1.46206E 03
$M_{H_2}$	9.04412E -01	9.05950E -01	9.74216E -01	9.75299E -01	9.78170E -01	9.81261E -01	9.80041E -01
$M_{H_2O}$	1.05329E 00	1.05182E 00	1.05304E 00	1.05075E 00	1.05036E 00	1.04528E 00	1.04113E 00
$M_{H_2O_2}$	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00
$P_{NS}/P'$	2.92261E 01	2.99359E 01	3.15950E 01	3.23001E 01	3.29052E 01	3.45010E 01	3.63631E 01
$P_{NS}/P'$	5.12920E 00	5.14992E 00	5.19516E 00	5.21510E 00	5.23009E 00	5.26549E 00	5.30507E 00
$T_{NS}$ DEG K	1.70937E 03	1.74340E 03	1.82453E 03	1.85275E 03	1.89205E 03	1.96573E 03	2.05519E 03
$M_{NS}$	4.16772E -01	4.09921E -01	4.00075E -01	4.07366E -01	4.06604E -01	4.05234E -01	4.03491E -01
$P_{NS}$ ATMOS	7.23097E 01	1.49017E 02	7.94750E 02	1.03173E 03	3.34571E 03	1.76403E 04	1.07490E 05

TABLE 12. CALCULATED DETONATION PARAMETERS FOR  $H_2 - O_2 - CO_2$  MIXTURES  
 $(2H_2 + O_2) + CO_2$   
 66 2/3 %  $H_2$  IN THE BASIC (STOICHIOMETRIC)  $H_2 - O_2$  MIXTURE (BY VOLUME) 25 %  $CO_2$   
 INITIAL TEMPERATURE 300° K  
 $n' = 4$  GM. MOLES  $m' = 20.0885$   $\gamma' = 3.73730$   $a_0' = 412.5482$  METERS PER SEC

DETONATION PARAMETERS	INITIAL PRESSURE, ATMOSPHERES							
	0.5	1	5	10	20	100	1000	
$T''$ DEG K	3.01425E 03	3.00055E 03	3.26370E 03	3.34001E 03	3.41359E 03	3.54180E 03	3.79350E 03	
$P'' / P'$	1.53717E 01	1.54457E 01	1.62279E 01	1.65049E 01	1.68054E 01	1.72520E 01	1.78901E 01	
$P' / P''$	5.43957E -01	5.44255E -01	5.46349E -01	5.46300E -01	5.46405E -01	5.46644E -01	5.46401E -01	
$P' / P''$ GM/CM <sup>2</sup>	4.04457E -04	4.12910E -04	4.04457E -03	4.12910E -03	4.12503E -02	4.12910E -02	4.12910E -01	
$m'' / m'$	1.20140E 00	1.20902E 00	1.22706E 00	1.23566E 00	1.24305E 00	1.26134E 00	1.28340E 00	
$D$ METERS / SEC	1.98200E 03	2.00146E 03	2.04554E 03	2.06397E 03	2.08125E 03	2.11044E 03	2.14230E 03	
$M'$	4.00430E 00	4.05155E 00	4.95045E 00	5.00307E 00	5.04464E 00	5.12540E 00	5.24271E 00	
$P''$ ATMOS	1.32103E 01	2.49094E 01	1.39361E 02	2.83017E 02	5.71835E 02	2.96209E 03	3.07641E 04	
$n''$ GM. MOLES	3.32079E 00	3.30045E 00	3.25902E 00	3.23072E 00	3.21708E 00	3.17123E 00	3.11340E 00	
$X_{H_2}$	3.79590E -12	5.75421E -12	1.59716E -11	1.95716E -11	2.54997E -11	4.13331E -11	5.71561E -11	
$X_{O_2}$	0.	0.	0.	0.	0.	0.	0.	
$X_{CO_2}$	1.03757E -10	2.01671E -10	2.34640E -17	5.57313E -17	1.10996E -16	5.08259E -16	2.99634E -15	
$X_{H_2O}$	0.92122E -23	3.63704E -22	7.54015E -21	2.64113E -20	8.20590E -20	9.33544E -19	1.47603E -17	
$X_{CO}$	0.19215E -13	1.54940E -12	5.94500E -12	1.02190E -11	1.62095E -11	4.25640E -11	1.00010E -10	
$X_{H_2O}$	2.42041E -11	5.03659E -11	2.07524E -10	3.70049E -10	6.25499E -10	1.93111E -09	6.93931E -09	
$X_{H_2O}$	1.13141E -12	2.60104E -12	1.62073E -11	3.50040E -11	7.14021E -11	3.47333E -10	2.62944E -09	
$X_{H_2O}$	3.48234E -13	8.97572E -13	7.51605E -12	1.04363E -11	4.31106E -11	2.94100E -10	3.57733E -09	
$X_{H_2O}$	5.67002E -10	1.04152E -15	1.72305E -16	4.53042E -16	1.12440E -15	8.15525E -13	9.15490E -12	
$X_{H_2O}$	5.60155E -20	2.63043E -19	8.17422E -18	3.47796E -17	1.36840E -16	2.97231E -15	1.58494E -13	
$X_{H_2O}$	4.99641E -04	7.35220E -04	1.69634E -05	2.50402E -05	3.27110E -05	6.36010E -05	1.37620E -04	
$X_{H_2O}$	1.03930E -01	1.00234E -01	8.94944E -02	8.39740E -02	7.05590E -02	4.47522E -02	4.46134E -02	
$X_{H_2O}$	1.94474E -01	2.01994E -01	2.17254E -01	2.24766E -01	2.32171E -01	2.50519E -01	2.76610E -01	
$X_{H_2O}$	1.16717E -02	9.83354E -03	6.35040E -03	5.10404E -03	4.12225E -03	2.33504E -03	8.99040E -04	
$X_{H_2O}$	3.00459E -02	3.54620E -02	2.90062E -02	2.72790E -02	2.45949E -02	1.89094E -02	1.19705E -02	
$X_{H_2O}$	5.20902E -01	5.34910E -01	5.56120E -01	5.60441E -01	5.73066E -01	5.92531E -01	6.17527E -01	
$X_{H_2O}$	1.00264E -02	8.77134E -03	6.14504E -03	5.16444E -03	4.26402E -03	2.50170E -03	1.04005E -03	
$X_{H_2O}$	5.54001E -02	5.20240E -02	4.59723E -02	4.27540E -02	3.96104E -02	3.20440E -02	2.17250E -02	
$X_{H_2O}$	3.05574E -00	4.63290E -00	1.16229E -07	1.67240E -07	2.37225E -07	4.94404E -07	1.16301E -06	
$X_{H_2O}$	5.48649E -02	5.26411E -02	4.60304E -02	4.64054E -02	4.35475E -02	3.64197E -02	2.34407E -02	
$X_{H_2O}$	2.40450E 01	2.41934E 01	2.45545E 01	2.47145E 01	2.48746E 01	2.52403E 01	2.57233E 01	
$Y_{H_2}$	1.19164E 00	1.18952E 00	1.18455E 00	1.18243E 00	1.18043E 00	1.17600E 00	1.17057E 00	
$Y_{H_2O}$	1.04002E 00	1.04291E 00	1.04050E 00	1.03140E 00	1.02430E 00	1.01544E 00	1.00362E 00	
$Y_{H_2O}$	1.11510E 00	1.11700E 00	1.13012E 00	1.13110E 00	1.14251E 00	1.14519E 00	1.15200E 00	
$u_{H_2}$ METERS / SEC	1.11440E 03	1.12367E 03	1.14410E 03	1.15202E 03	1.16057E 03	1.17794E 03	1.19004E 03	
$u_{H_2O}$ METERS / SEC	1.02701E 03	1.03073E 03	1.04300E 03	1.07444E 03	1.08471E 03	1.10004E 03	1.13007E 03	
$u_{H_2O}$ METERS / SEC	1.07012E 03	1.08931E 03	1.11799E 03	1.12734E 03	1.14170E 03	1.16243E 03	1.18054E 03	
$u_{H_2O}$ METERS / SEC	1.07014E 03	1.08934E 03	1.11736E 03	1.12750E 03	1.14162E 03	1.16244E 03	1.18059E 03	
$M_{H_2}$	9.67407E -01	9.69451E -01	9.76705E -01	9.78162E -01	9.83040E -01	9.86043E -01	9.92101E -01	
$M_{H_2O}$	1.04890E 00	1.04873E 00	1.05059E 00	1.04925E 00	1.05265E 00	1.04912E 00	1.04404E 00	
$M_{H_2O}$	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	1.00003E 00	
$P_{NS} / P'$	2.44924E 01	2.70183E 01	2.82209E 01	2.87420E 01	2.92200E 01	3.02932E 01	3.15493E 01	
$P_{NS} / P'$	5.23340E 00	5.25309E 00	5.29572E 00	5.31290E 00	5.32072E 00	5.36193E 00	5.39924E 00	
$T_{NS}$ DEG K	1.51859E 03	1.54299E 03	1.59915E 03	1.62294E 03	1.64550E 03	1.69490E 03	1.75449E 03	
$M_{NS}$	4.00015E -01	4.07234E -01	4.05543E -01	4.04867E -01	4.04247E -01	4.02950E -01	4.01520E -01	
$P_{NS}$ ATMOS	6.67003E 01	1.36674E 02	1.20904E 02	1.47391E 03	3.00030E 03	1.57000E 04	1.65052E 05	

**Appendix IX.**  
**Experimental Values of Detonation Velocity and Pressure**



TABLE 14. - EXPERIMENTAL WAVE PROPAGATION TIMES AND EXPERIMENTAL AND THEORETICAL DETONATION VELOCITIES AND PRESSURES FOR STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADDED WITH INERT GASELS AT VARIOUS INITIAL PRESSURES AND AT 50 MPa INITIAL TEMPERATURE

[illegible]





TABLE IV. - EXPERIMENTAL WAVE PROPAGATION TIMES AND EXPERIMENTAL AND THEORETICAL RETONATION VELOCITIES AND PRESSURES FOR STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADDED WITH 3% HELIUM AT VARIOUS INITIAL PRESSURES AND AT 300K INITIAL TEMPERATURE

[illegible]



TABLE 18. - EXPERIMENTAL WAVE PROPAGATION TIMES AND EXPERIMENTAL AND THEORETICAL DETONATION VELOCITIES AND PRESSURES FOR STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADJUSTED WITH ARGON AT VARIOUS INITIAL PRESSURES AND AT 200K INITIAL TEMPERATURE

Mixture	Argon in mole %	Average time of wave, $\mu$ sec					Experimental wave velocity, m/sec					Experimental pressure, MPa					Theoretical pressure, MPa				
		1-27, 1000, 10000, 100000, 1000000					1000, 10000, 100000, 1000000, 10000000					1000, 10000, 100000, 1000000, 10000000					1000, 10000, 100000, 1000000, 10000000				
		1-27	1000	10000	100000	1000000	1000	10000	100000	1000000	10000000	1000	10000	100000	1000000	10000000	1000	10000	100000	1000000	10000000
$H_2/O_2 = 1/1$ (4.0:1)	1	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	2	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	4	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
$H_2/O_2 = 1/2$ (2.0:1)	1	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	2	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	4	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
$H_2/O_2 = 1/3$ (1.33:1)	1	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	2	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	4	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
$H_2/O_2 = 1/4$ (1.0:1)	1	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	2	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	4	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

1. Calculated from data of Table 17.  
2. Calculated from data of Table 17.  
3. Calculated from data of Table 17.  
4. Calculated from data of Table 17.

[illegible]

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[illegible]

1970-1971

TABLE 2. - EXPERIMENTAL WAVE PROPAGATION TIMES AND EXPERIMENTAL AND THEORETICAL RETONATION VELOCITIES AND PRESSURES FOR STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADMIXED WITH 4% CARBON BIKRIDE AT VARIOUS INITIAL PRESSURES AND AT 300K INITIAL TEMPERATURE

[illegible]

\* Interpolated from Graph Fig.  
Interpolated from Graph Fig.  
Estimated by interpolation of  
known points of known (in)

[illegible]

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TABLE 3A. - EXPERIMENTAL WAVE PROPAGATION TIMES AND EXPERIMENTAL AND THEORETICAL IGNITION VELOCITIES AND PRESSURES FOR STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADMIXED WITH 2% CARBON DIOXIDE AT VARIOUS INITIAL PRESSURES AND AT 2000 K INITIAL TEMPERATURE

Series	Run No.	Initial Pressure (mm Hg)	Experimental Wave Propagation Times (ms)					Experimental Ignition Velocities (cm/sec)					Experimental Ignition Pressures (mm Hg)					Theoretical Ignition Pressures (mm Hg)					Theoretical Ignition Velocities (cm/sec)					Remarks	
			Series 1					Series 2					Series 3					Series 4					Series 5						
			2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K	2000 K		
			1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
1	1	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	2	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	3	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	4	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	5	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	6	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	7	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	8	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	10	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
2	11	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	12	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	13	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	14	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	15	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	16	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	17	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	18	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	19	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	20	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		
	21	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000		

1. Ignition velocity (cm/sec)

Appendix X.  
Theoretical and Experimental Values of  
Detonation Parameters Obtained from Literature

TABLE 25 LITERATURE VALUES OF THEORETICAL AND EXPERIMENTAL DETONATION PARAMETERS FOR STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ARMED WITH HELIUM, ARGON, OR CARBON DIOXIDE

[illegible]

\* Inexplicably inconsistent from experimental phase

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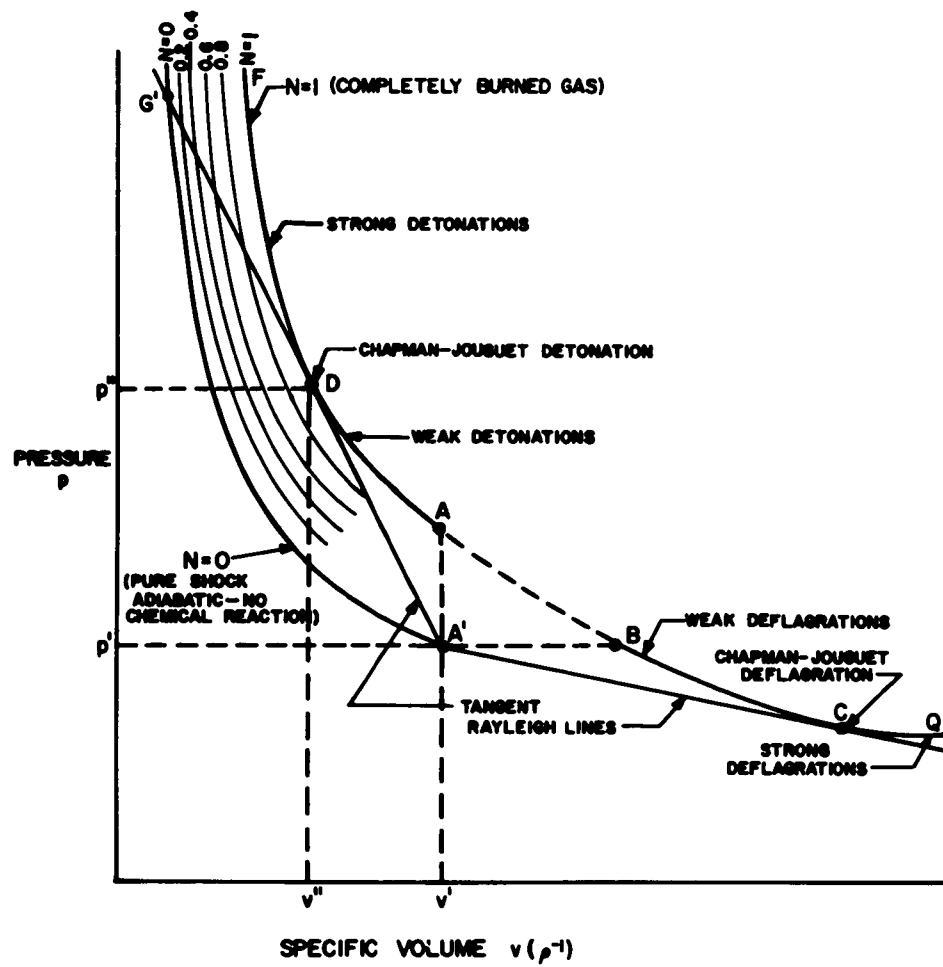


FIGURE 1 HUGONIOT DIAGRAM



FIG. 2 OVERALL VIEW OF HIGH-PRESSURE DETONATION INSTALLATION IN TEST CELL



FIG. 3 MAIN CONTROL AND INSTRUMENTATION CONSOLE IN CONTROL ROOM

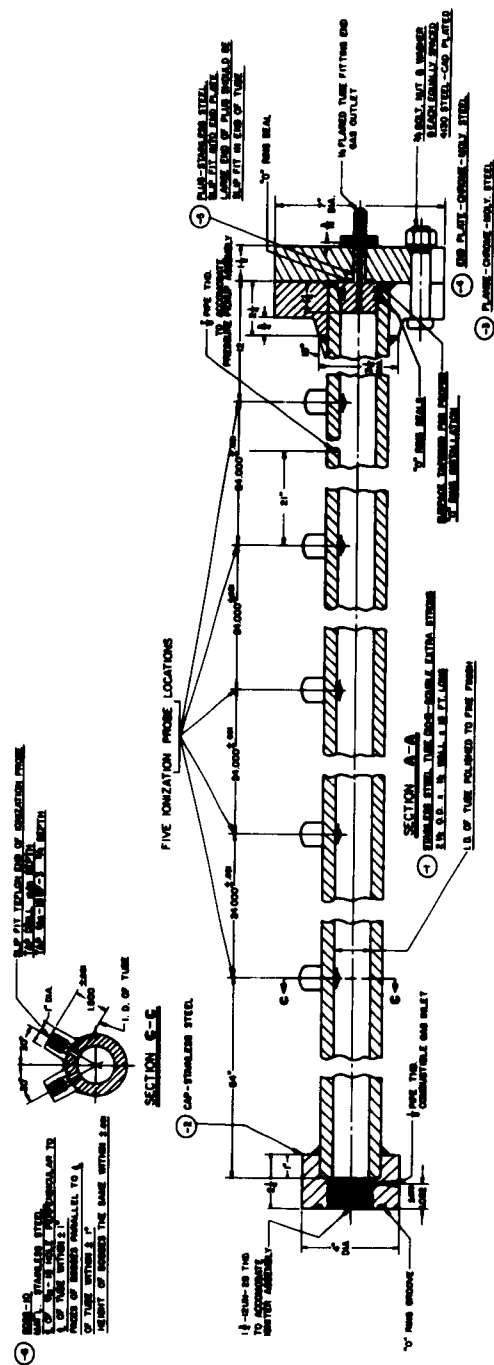


FIG. 4 HIGH PRESSURE DETONATION TUBE ASSEMBLY



FIG. 5 DETONATION TUBE INSTALLED IN CONSTANT TEMPERATURE WATER BATH SHOWING IONIZATION PROBES, PRESSURE TRANSDUCER AND PRESSURE MEASURING EQUIPMENT

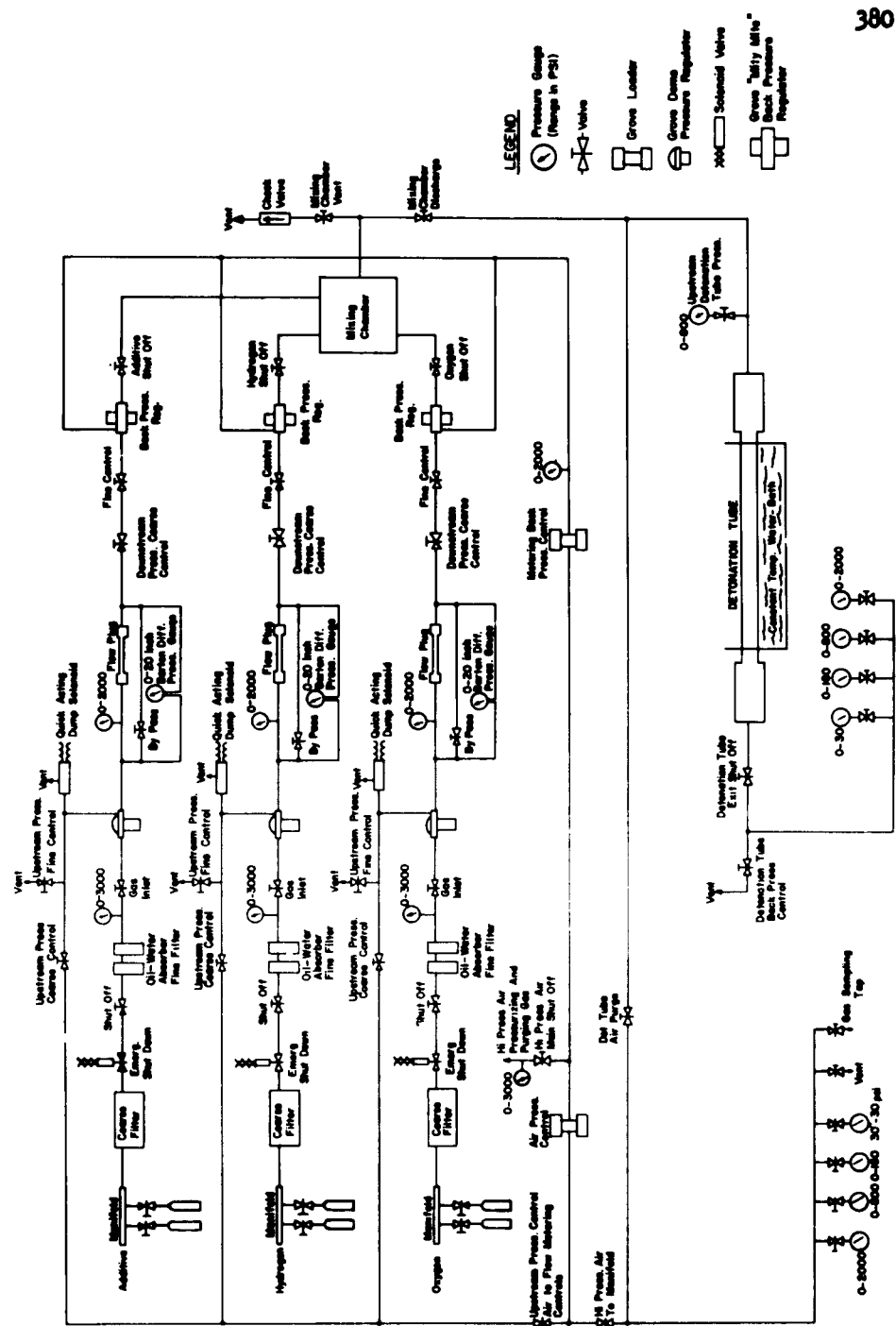


FIG. 6 HIGH PRESSURE DETONATION TEST INSTALLATION

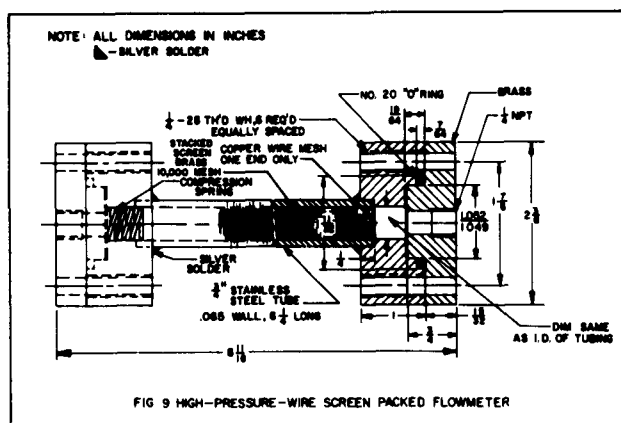


FIG. 7 DESIGN DETAILS OF HIGH-PRESSURE WIRE SCREEN PACKED FLOWMETER

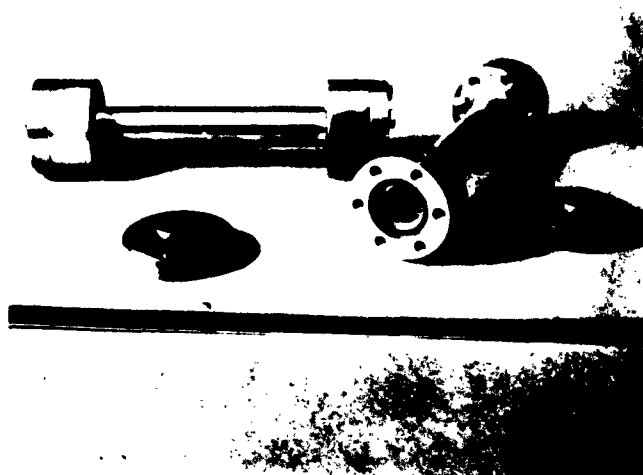


FIG. 8 EXPLODED VIEW OF PACKED FLOWMETER





FIG. 9 MIXING-ON-FLOW CONTROL EQUIPMENT RACK IN TEST CELL

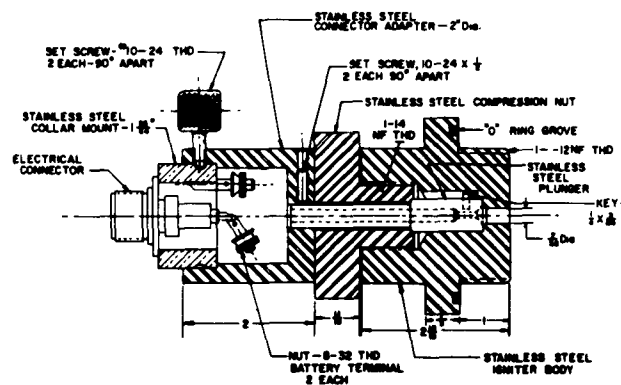


FIG. 10 DESIGN DETAILS OF HIGH-PRESSURE EXPLODING WIRE IGNITER

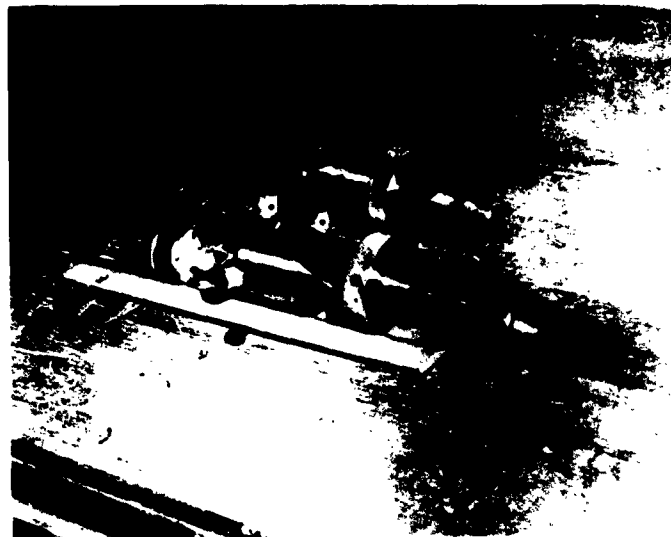


FIG. 11 EXPLODED VIEW OF HIGH-PRESSURE EXPLODING WIRE IGNITER



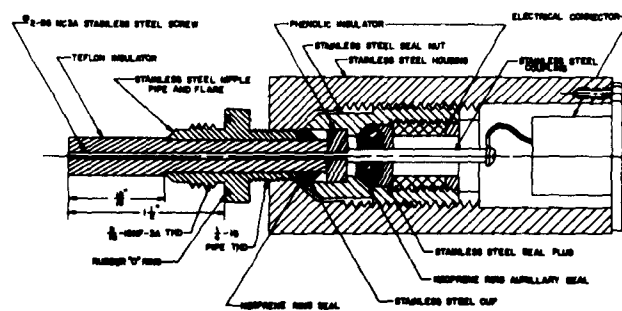


FIG. 13 DESIGN DETAILS OF HIGH-PRESSURE IONIZATION PROBE

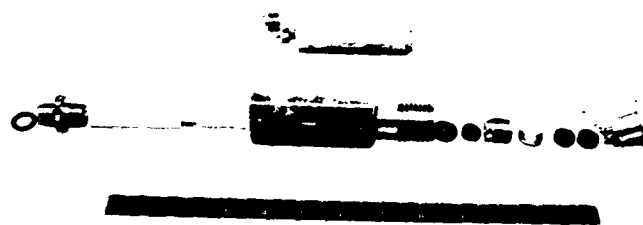


FIG. 14 EXPLODED AND ASSEMBLED VIEW OF IONIZATION PROBE



FIG. 15 IONIZATION PROBE AND PRESSURE TRANSDUCER INSTALLED IN DETONATION TUBE

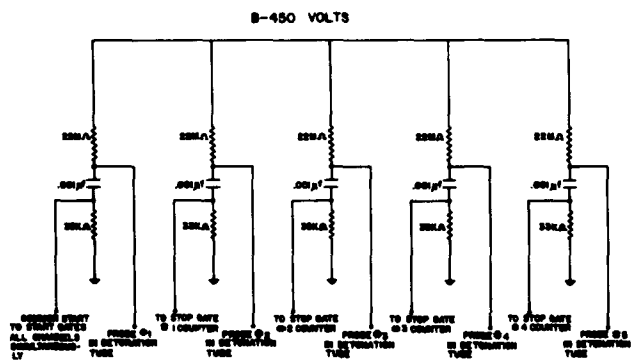
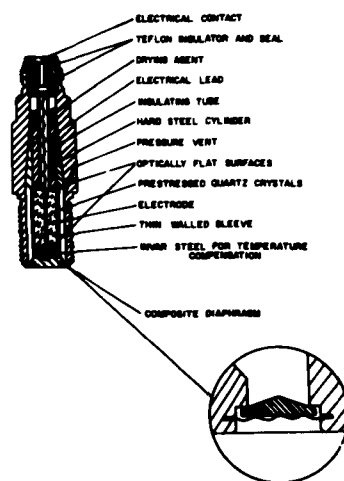
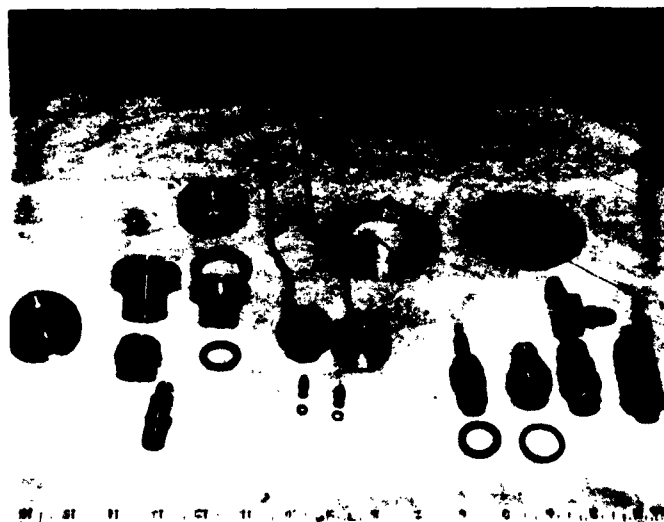


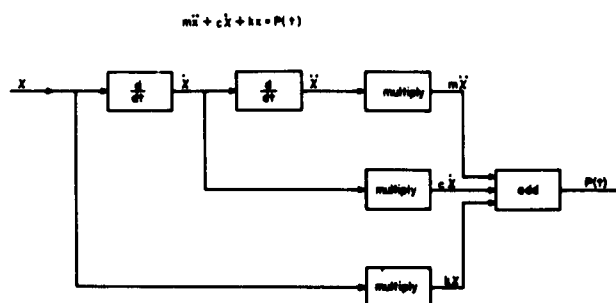
FIG. 16 SCHEMATIC WIRING DIAGRAM OF ELECTRONIC CHRONOGRAPH PULSE TRIGGERING CIRCUIT



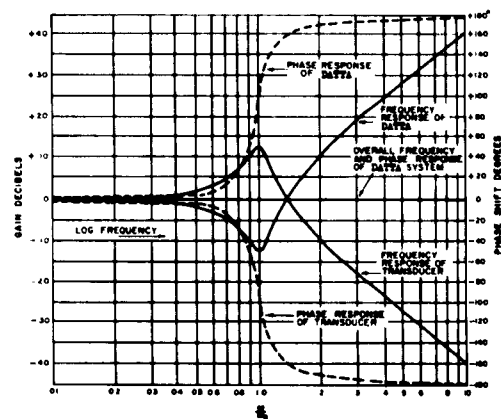
**FIG.17 DESIGN DETAILS OF KISTLER SLM PRESSURE GAGE**



**FIG.18 PHOTOGRAPH OF DIFFERENT TYPES OF PRESSURE TRANSDUCERS, AND RIGID AND SHOCK-TYPE TRANSDUCER MOUNTS TESTED**



**FIG 19** FUNCTIONAL DIAGRAM OF IDEALIZED DYNAMIC ANALOG COMPENSATOR



**FIG 20** FREQUENCY RESPONSE ANALYSIS OF DATA SYSTEM

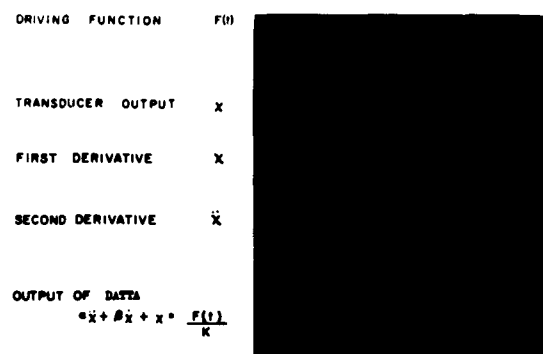


FIG 21 FUNCTIONAL PRESENTATION OF SIMULATED TRANSDUCER AND DATA SYSTEM

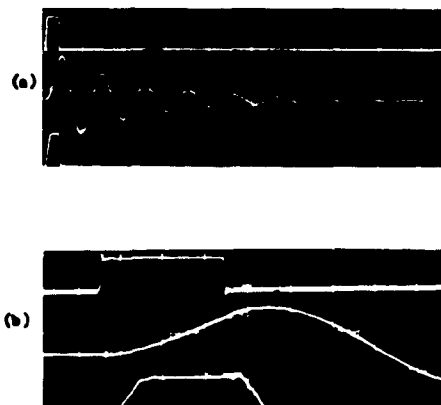


FIG 22 DRIVING FUNCTION, SIMULATED TRANSDUCER OUTPUT AND EQUILIZED DATA OUTPUT



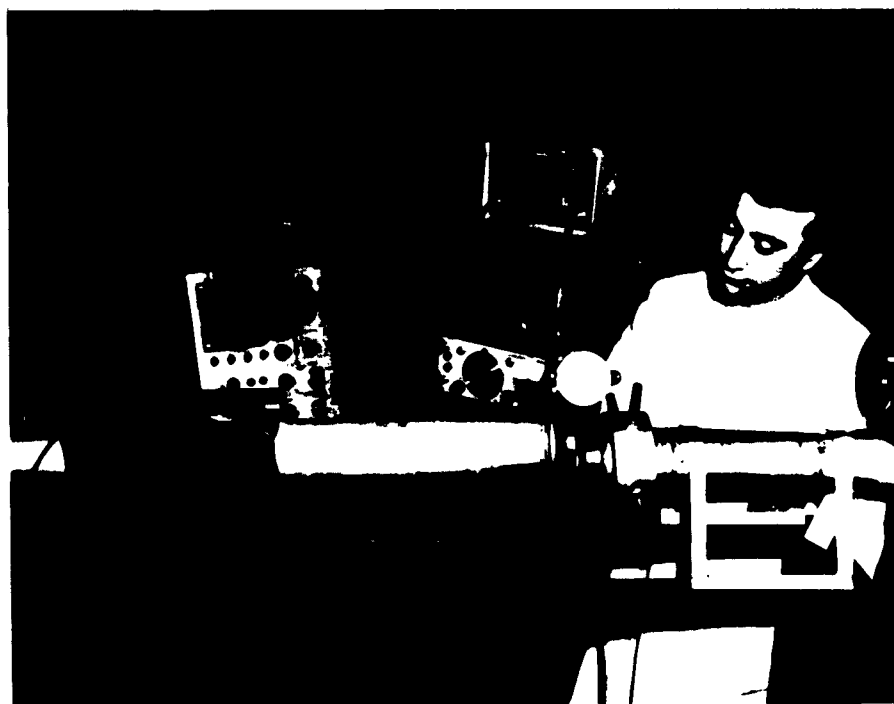
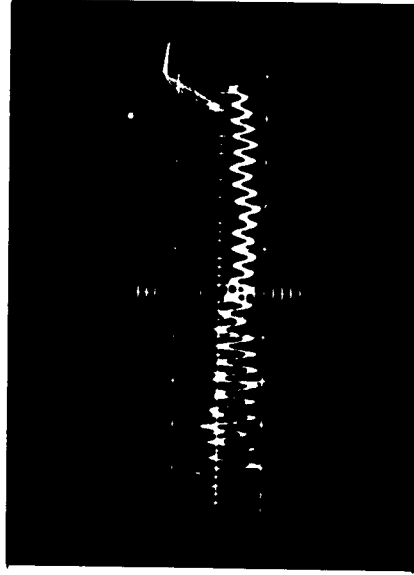


FIG 23 SHOCK TUBE AND ASSOCIATED INSTRUMENTATION



**SWEEP SPEED, 20 sec/div.**

**FIG. 24. TYPICAL OSCILLOSCOPE RECORD OF TRANSIENT  
RESPONSE OUTPUT DUE TO SHOCK-PRESSURE STEP FUNCTION OF  
KISTLER SLM MODEL 605 PIEZOELECTRIC PRESSURE TRANSDUCER  
( $\Delta P = 40 \text{ psia}$ ; Frequency = 133 kc; Damping Factor  $\approx 0.02$ )**

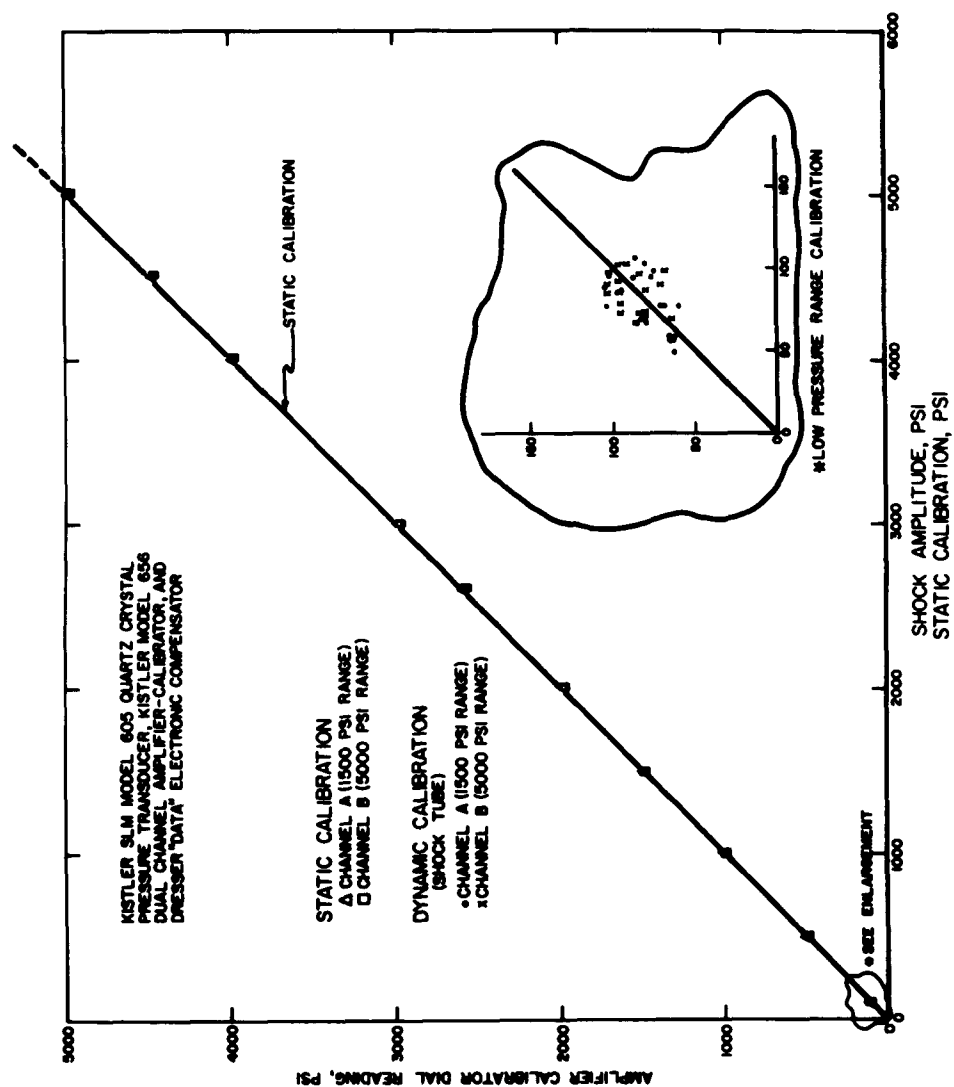


FIG. 25 CALIBRATION OF KISTLER SLM PIEZO ELECTRIC PRESSURE TRANSDUCER

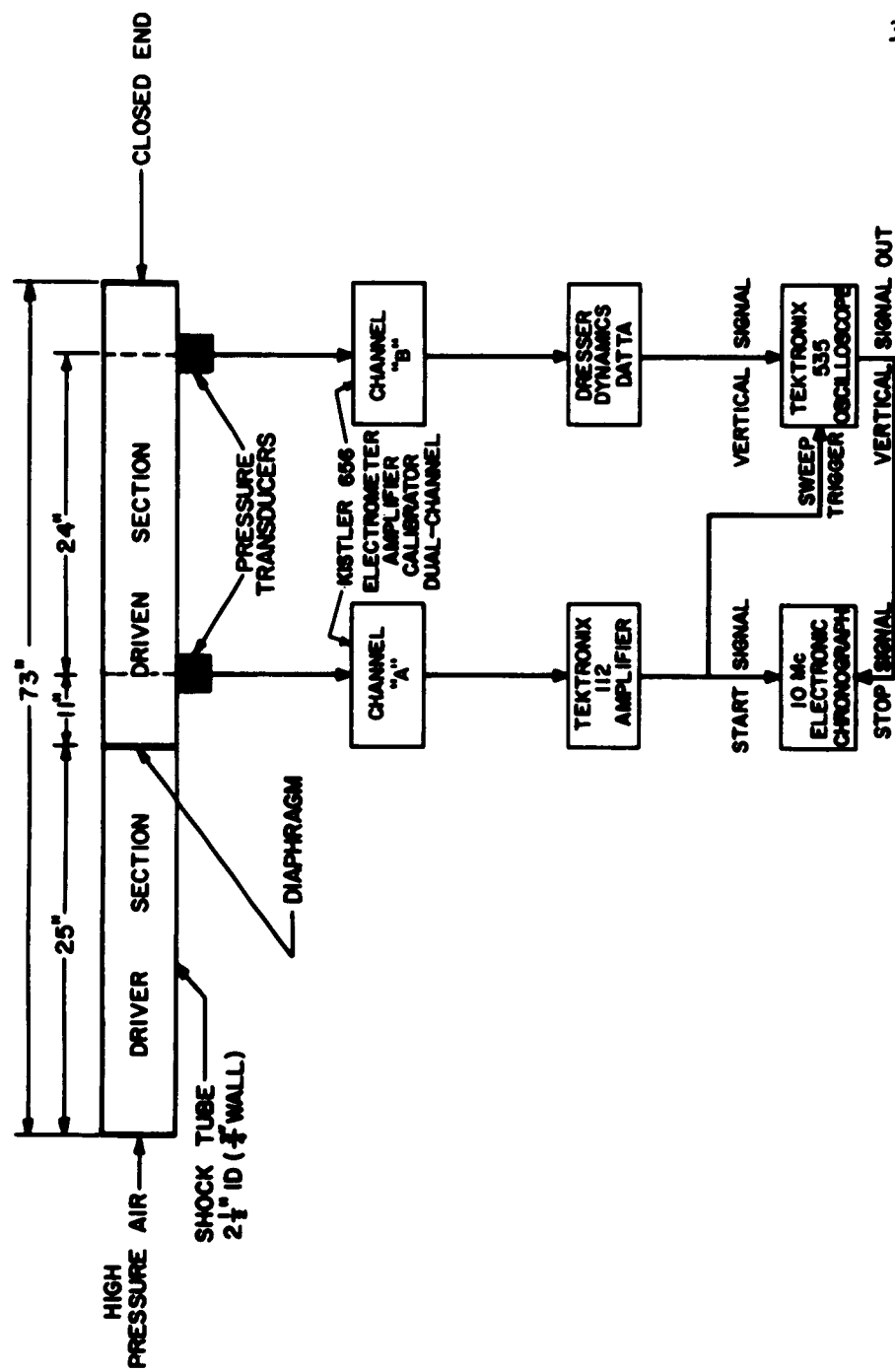
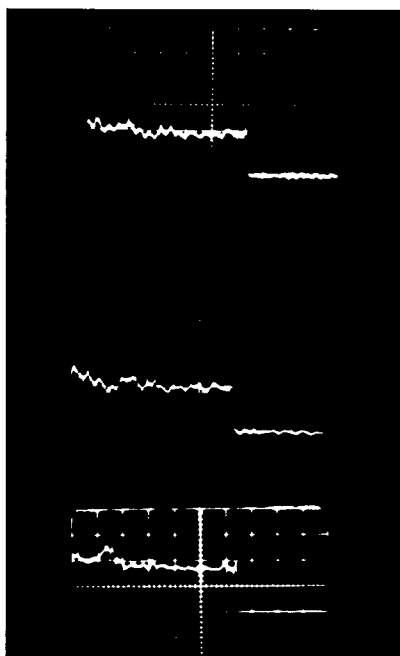


FIG. 26 BLOCK DIAGRAM OF PRESSURE TRANSDUCER CALIBRATION APPARATUS

GAGE RESPONSE FROM  
STATIC CALIBRATION  
96 psia.

GAGE RESPONSE FROM  
STATIC CALIBRATION  
102 psia.

GAGE RESPONSE FROM  
STATIC CALIBRATION  
103 psia.



SHOCK AMPLITUDE  
COMPUTED FROM SHOCK  
VELOCITY  
91.5 psia.

SHOCK AMPLITUDE  
COMPUTED FROM SHOCK  
VELOCITY  
96.3 psia.

SHOCK AMPLITUDE  
COMPUTED FROM SHOCK  
VELOCITY  
103 psia.

TIME, 200 sec./div.

FIG. 27 SHOCK WAVE RESPONSE OF KISTLER SLM  
MODEL 605 QUARTZ CRYSTAL PRESSURE PICKUP,  
AMPLIFIER-CALIBRATOR AND "DATT".

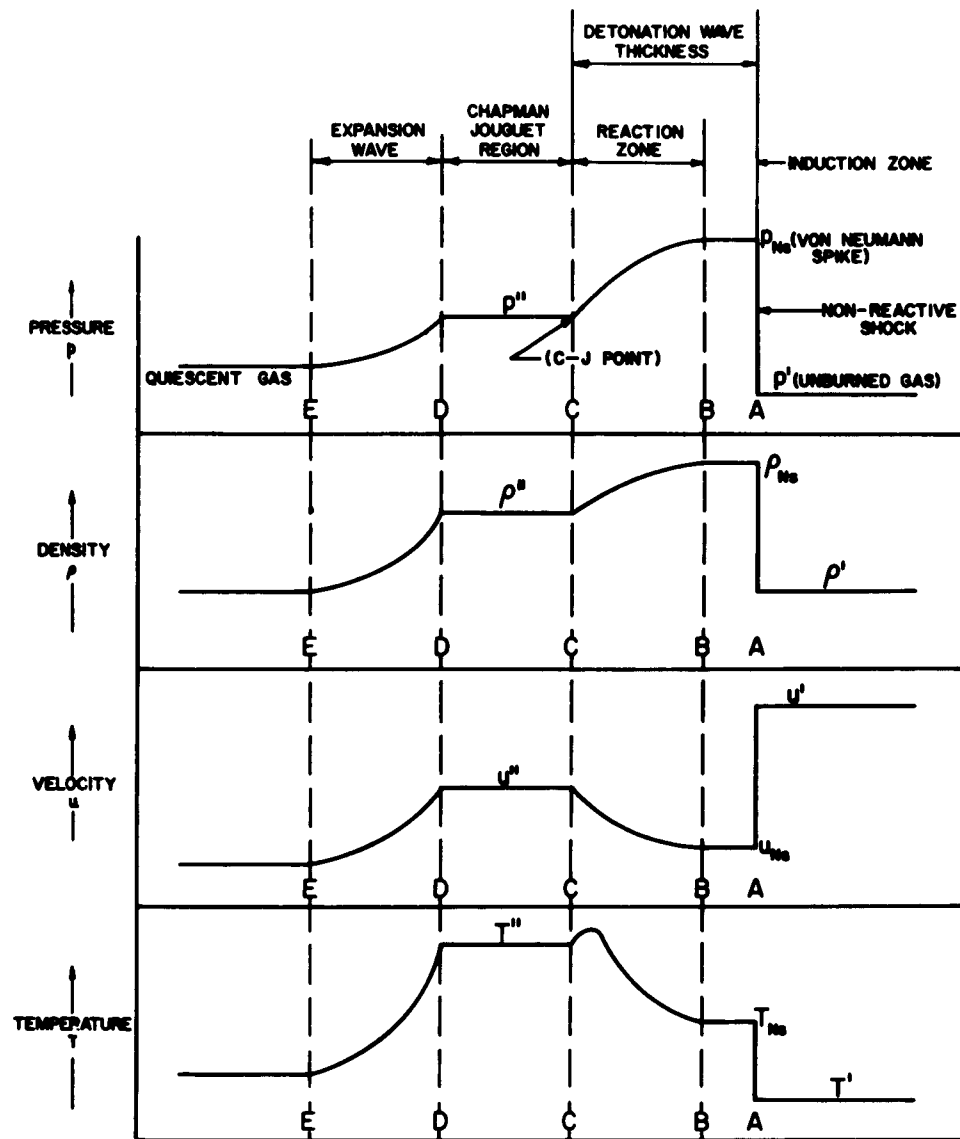


FIG 28 IDEALIZED REPRESENTATION OF THE STRUCTURE OF A ONE-DIMENSIONAL PLANE STEADY DETONATION WAVE

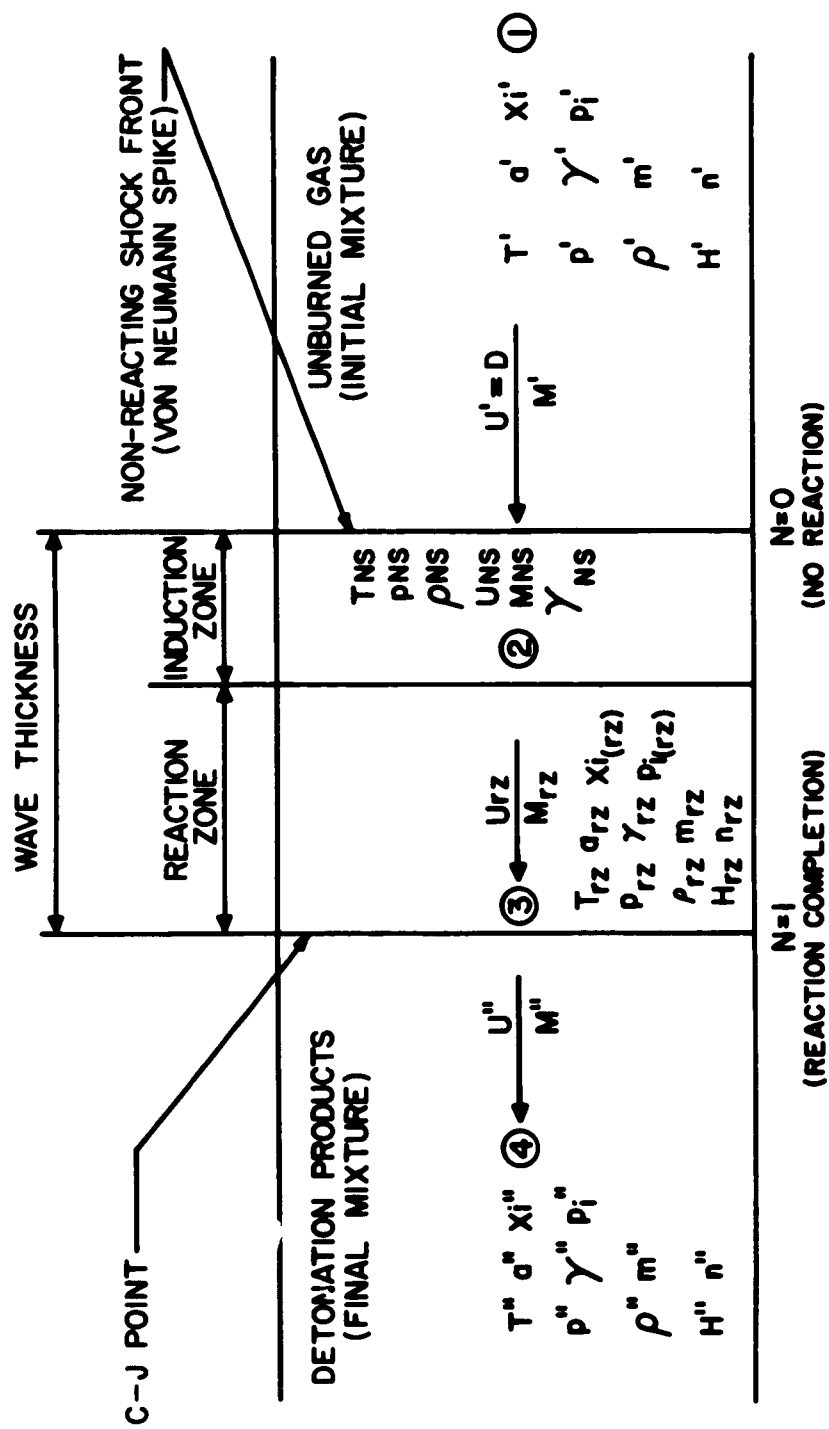
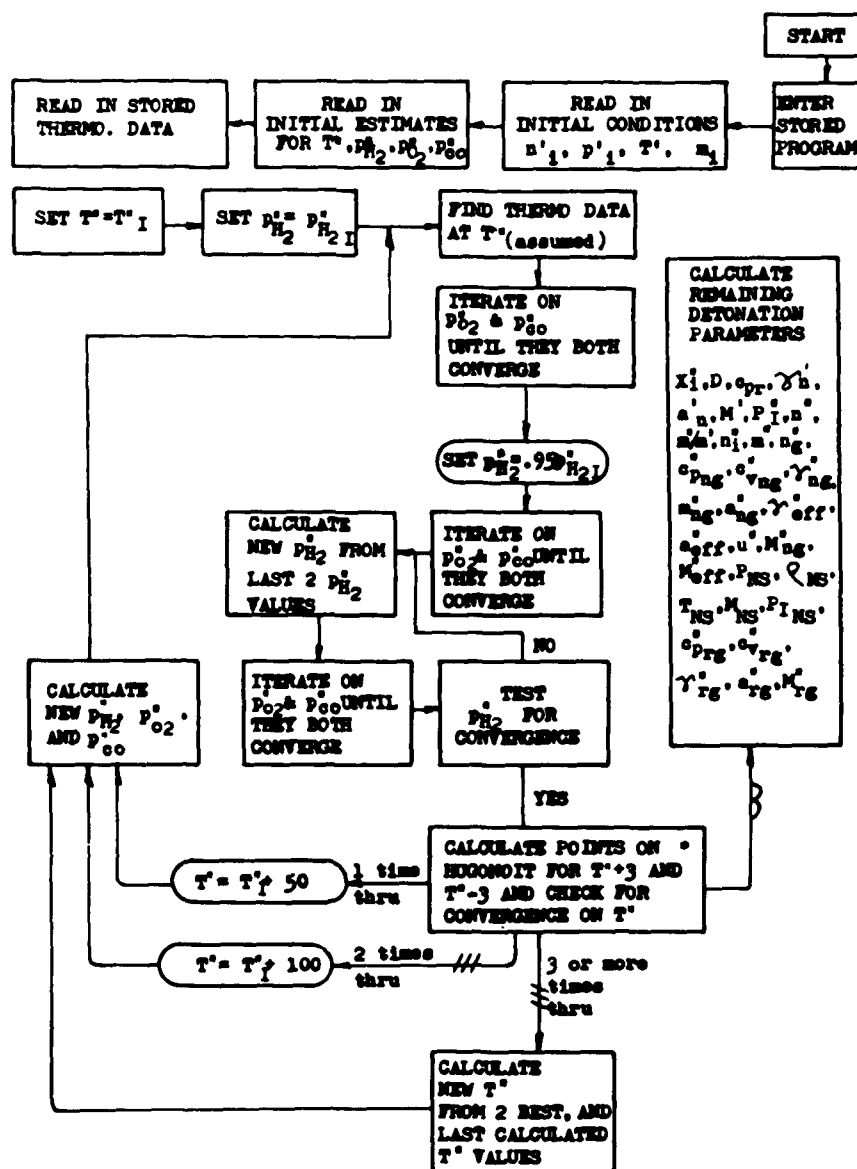


FIG.29 STANDING DETONATION WAVE REFERENCE SYSTEM



/// NO CONVERGENCE  
 CONVERGENCE HAS BEEN REACHED

- NOTE:
1. 'I' SUBSCRIPT MEANS INPUT VALUE OF THE PARAMETER.
  2. TO OBTAIN THE DESIRED POINTS ( $p^*/p'$ ,  $'/'$ ) ON THE HUGONIT IT IS NECESSARY TO PROCEED THROUGH THE ENTIRE ITERATION PROCEDURE UNTIL CONVERGENCE IS REACHED AT  $T^+ 3$  AND  $T^- 3$
  3.  $p_{CO} = 0$  WHEN  $CO_2$  IS NOT PRESENT IN THE INITIAL MIXTURE.

FIG. 30 GENERAL CALCULATION FLOW DIAGRAM



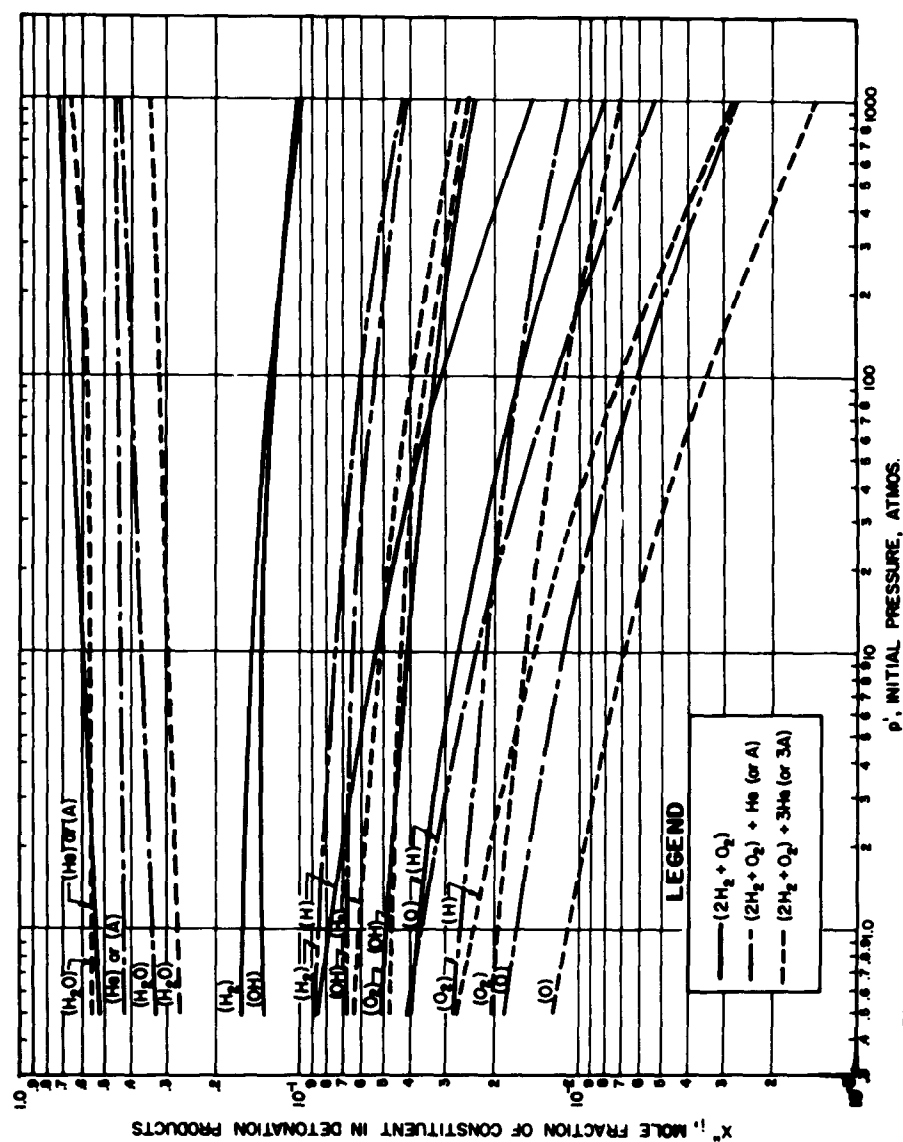


FIG. 31. VARIATION OF THEORETICAL DETONATION PRODUCT COMPOSITION WITH INITIAL PRESSURE AT 300°K. INITIAL TEMPERATURE FOR STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADMIXED WITH HELIUM OR ARGON.

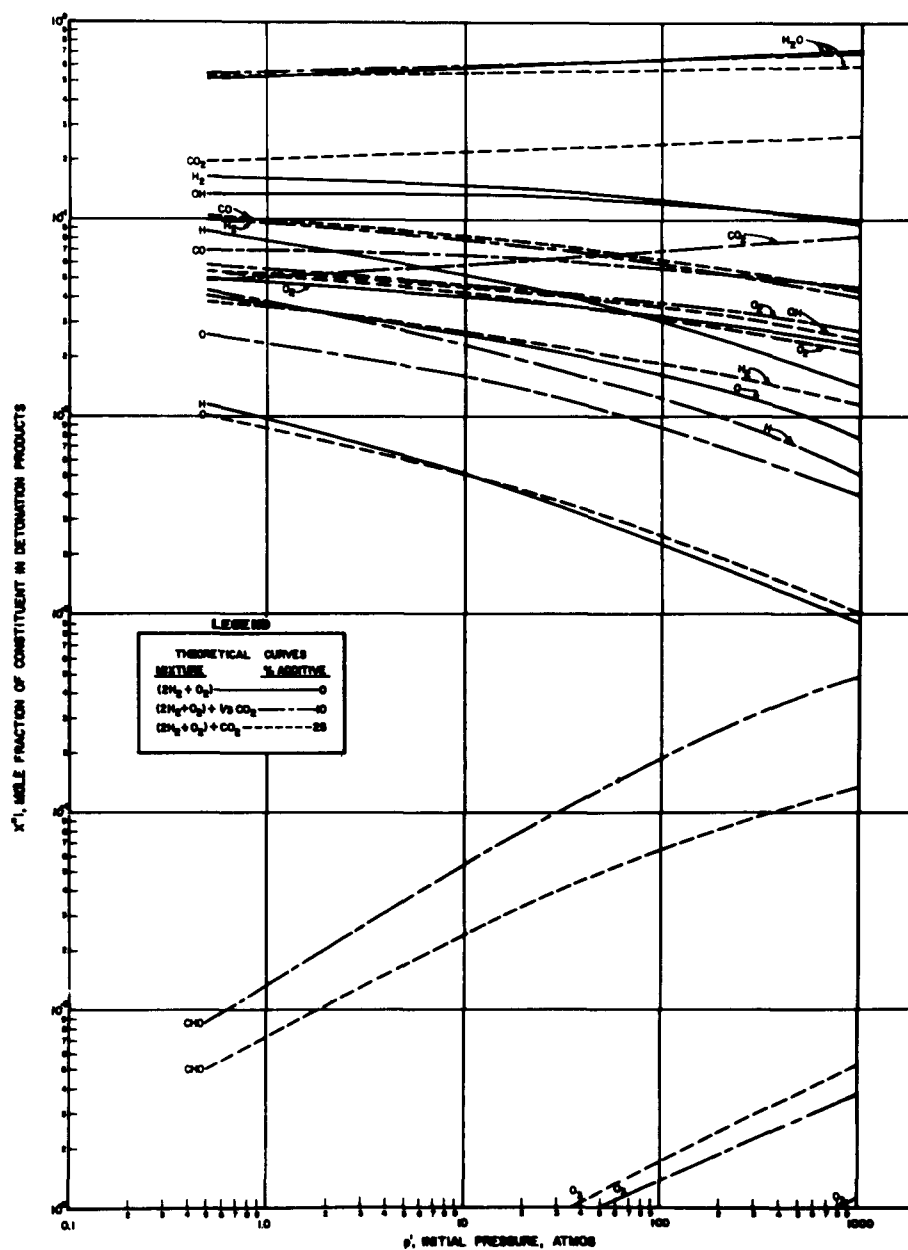


FIG. 32 VARIATION OF THEORETICAL DETONATION PRODUCT COMPOSITION WITH INITIAL PRESSURE AT 300°K INITIAL TEMPERATURE FOR STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADMIXED WITH CARBON DIOXIDE

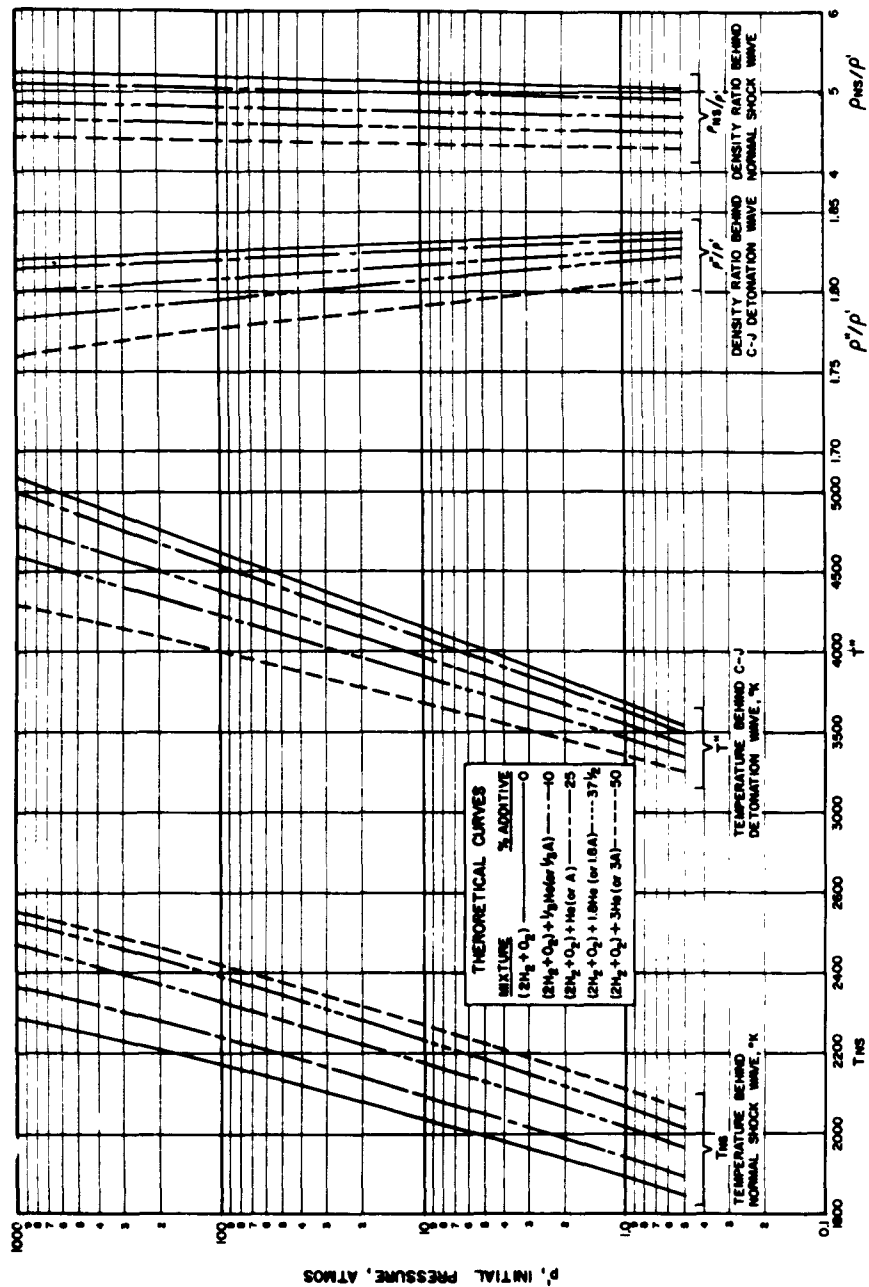


FIG. 33 VARIATION OF THEORETICAL DETONATION AND NORMAL SHOCK WAVE TEMPERATURES AND DENSITY RATIOS WITH INITIAL PRESSURE AT 300 °K INITIAL TEMPERATURE IN STOICHIOMETRIC HYDROGEN-OXYGEN ADMIXED WITH HELIUM OR ARGON.

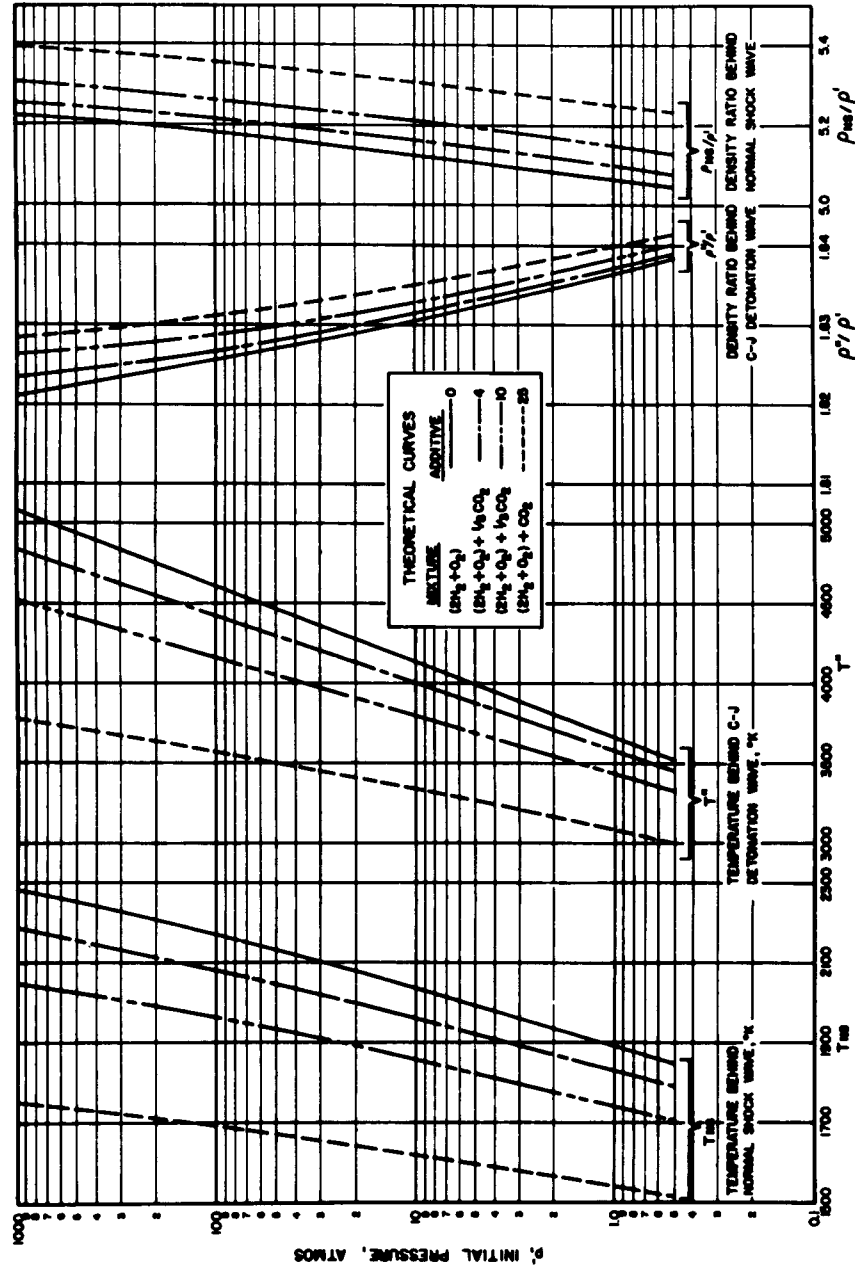


FIG. 3.4 VARIATION OF THEORETICAL DETONATION AND NORMAL SHOCK WAVE TEMPERATURES AND DENSITY RATIOS WITH INITIAL PRESSURE AT 300°K INITIAL TEMPERATURE IN STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADMIXED WITH CARBON DIOXIDE

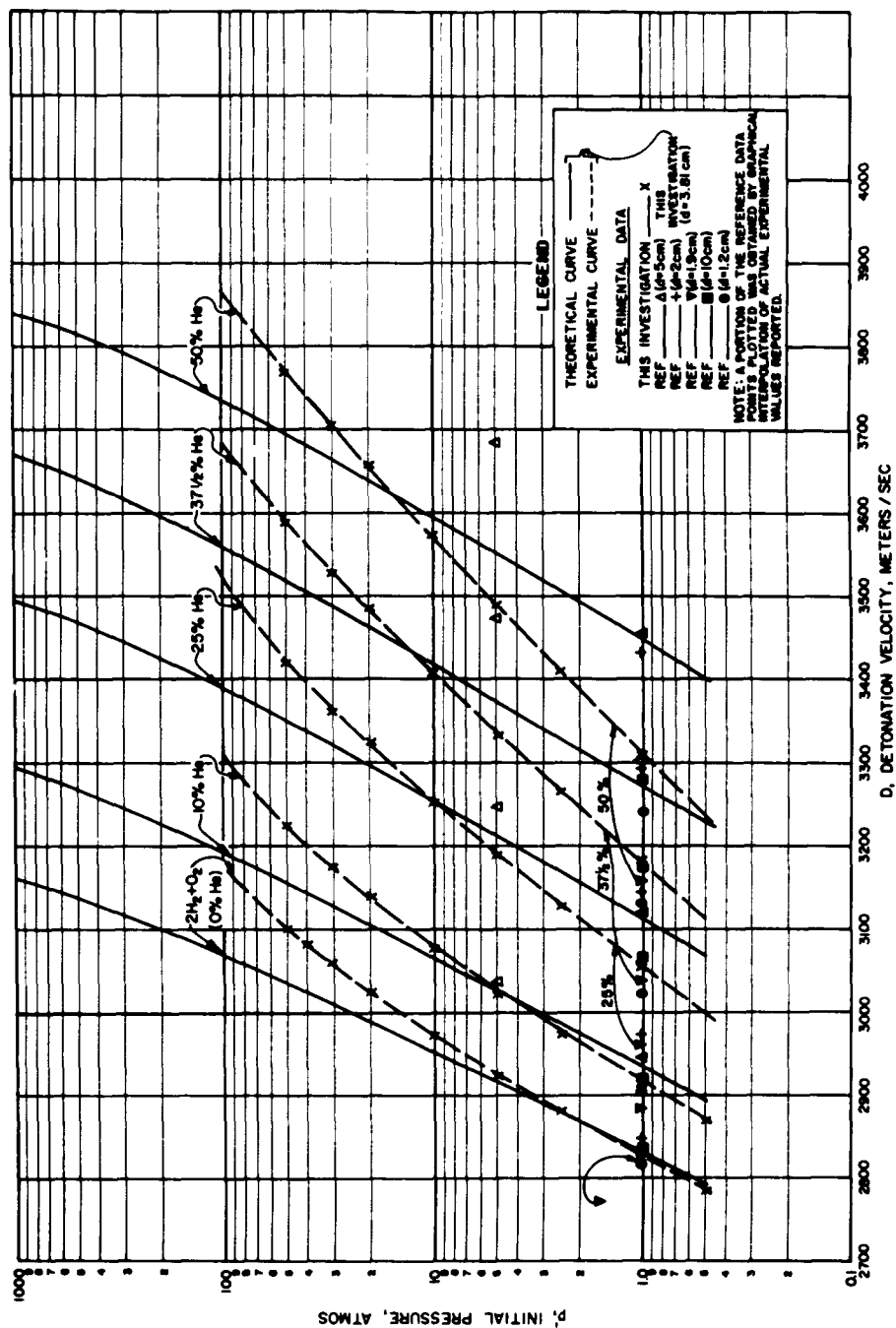


FIG. 35. VARIATION OF THEORETICAL AND EXPERIMENTAL DETONATION VELOCITY WITH INITIAL PRESSURE AT 300°K  
INITIAL TEMPERATURE FOR STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADMIXED WITH HELIUM.

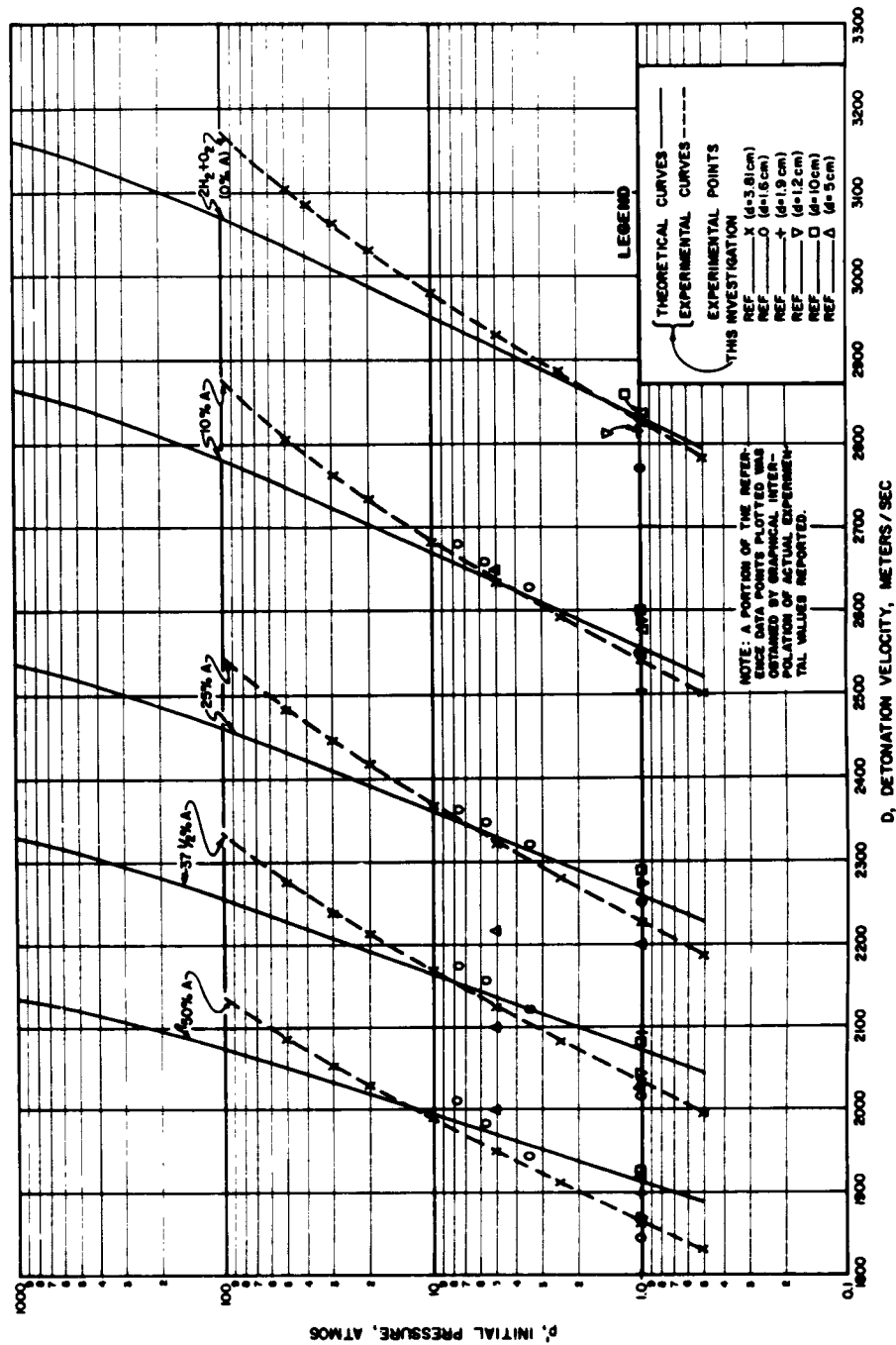


FIG. 36 VARIATION OF THEORETICAL AND EXPERIMENTAL DETONATION VELOCITY WITH INITIAL PRESSURE AT 300 °K  
 INITIAL TEMPERATURE FOR STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADMIXED WITH ARGON.

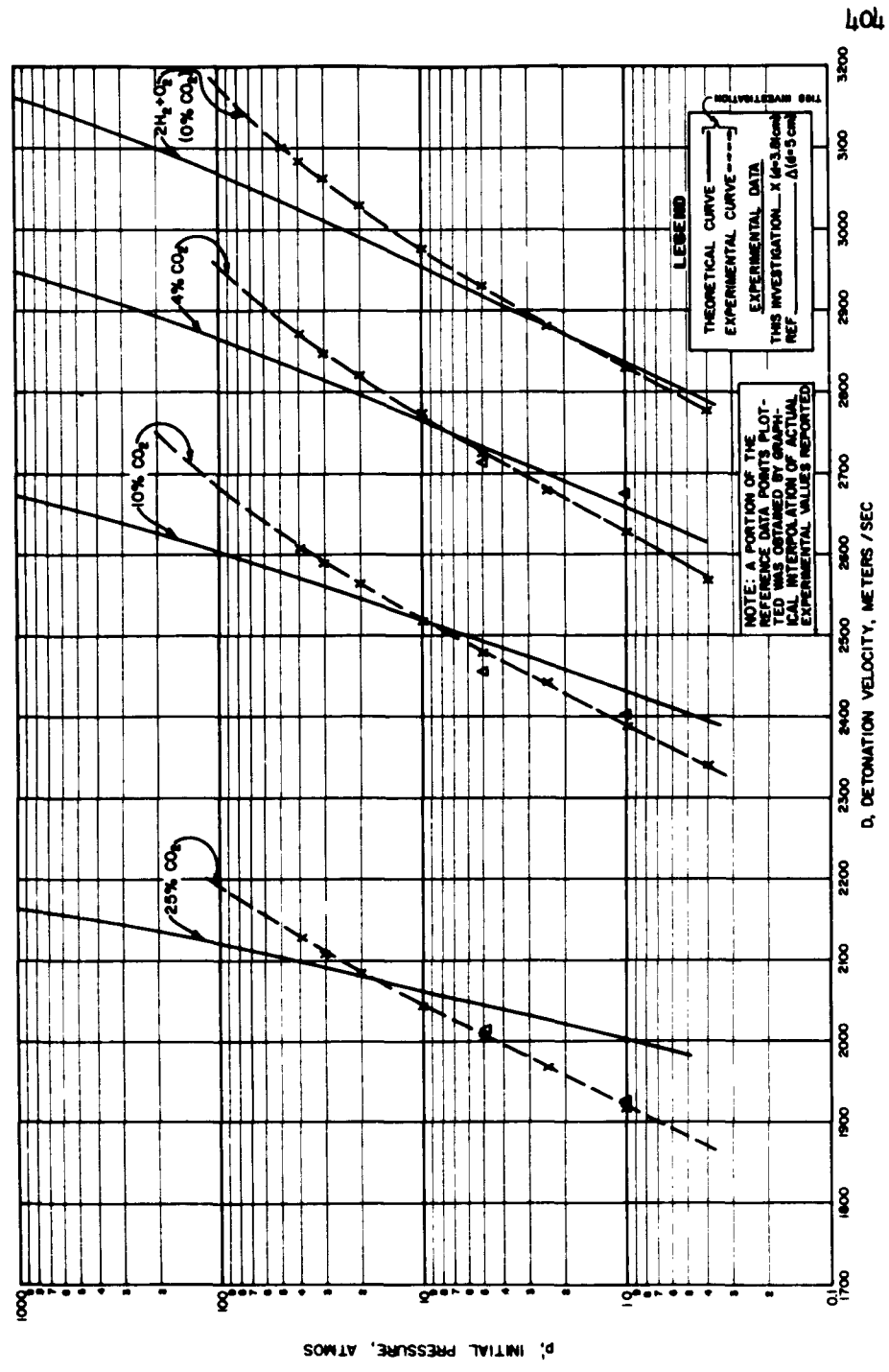


FIG. 37 VARIATION OF THEORETICAL AND EXPERIMENTAL DETONATION VELOCITY WITH INITIAL PRESSURE AT 300°K FOR STOICHIOMETRIC HYDROGEN—OXYGEN MIXTURES ADMIXED WITH CARBON DIOXIDE.

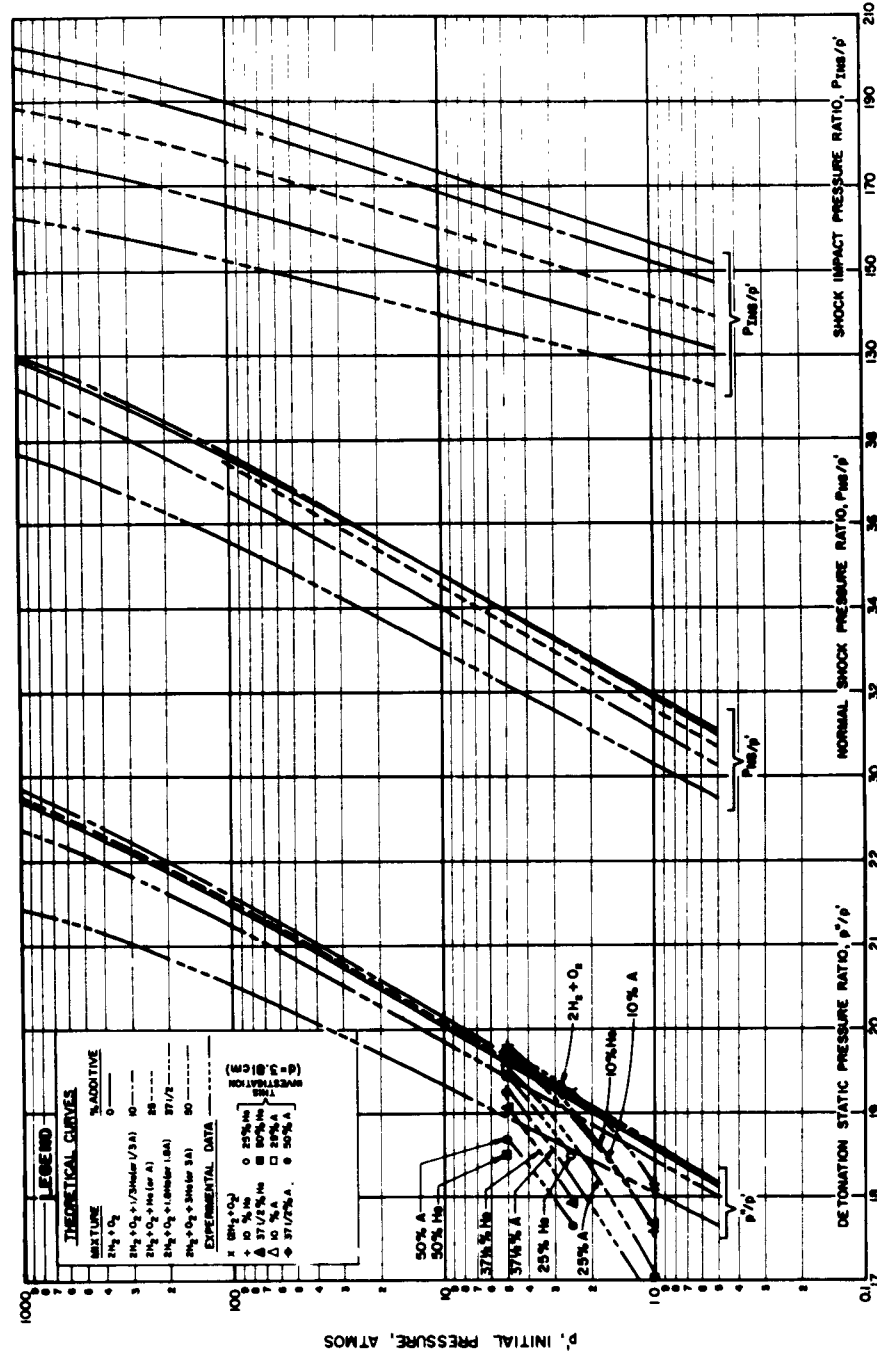


FIG. 38. VARIATION OF RATIOS OF DETONATION AND SHOCK WAVE PRESSURE TO INITIAL PRESSURE WITH INITIAL PRESSURE AT 300°K INITIAL TEMPERATURE IN STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADMIXED WITH HELIUM OR ARGON.



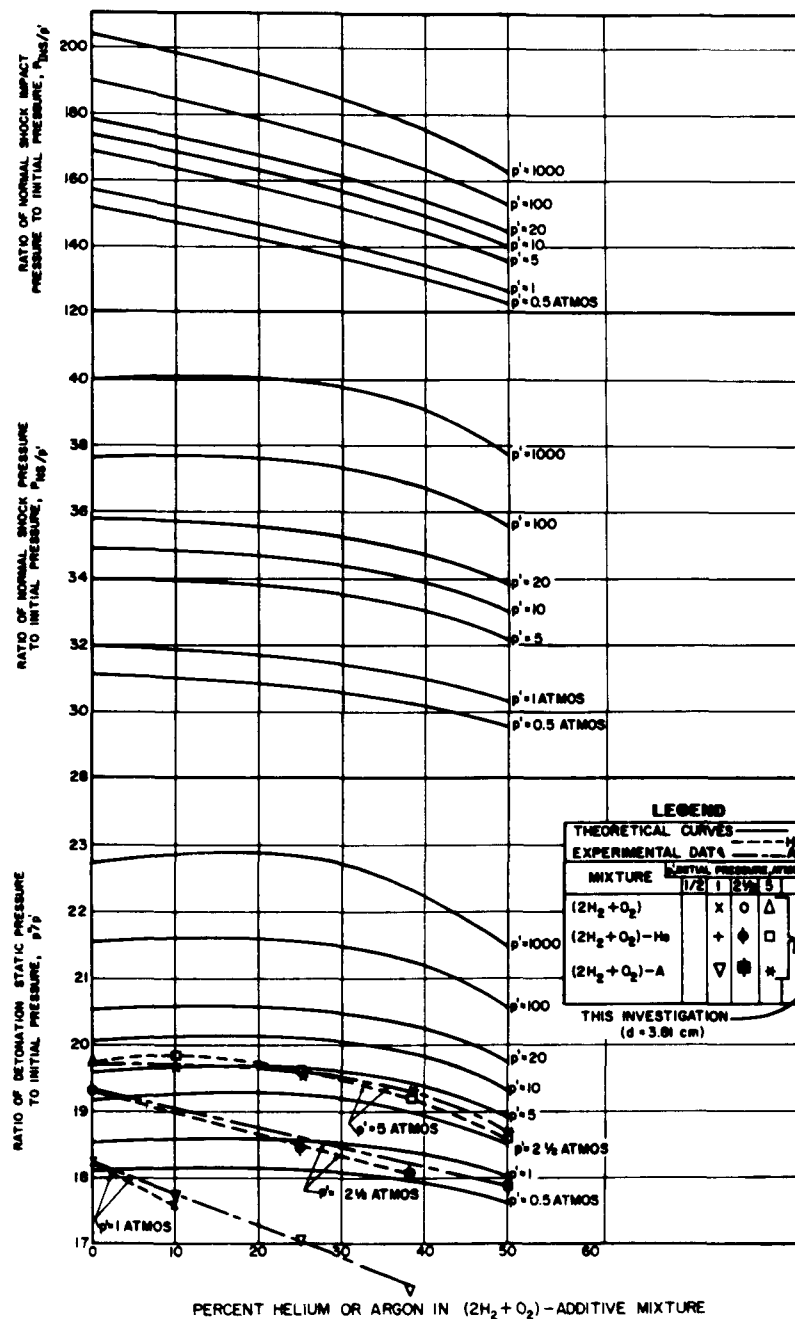


FIG. 39 VARIATION OF DETONATION AND SHOCK WAVE PRESSURE RATIOS WITH PERCENT ADDITIVE IN STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADMIXED WITH HELIUM OR ARGON AT VARIOUS INITIAL PRESSURES AND INITIAL TEMPERATURE OF 300°K

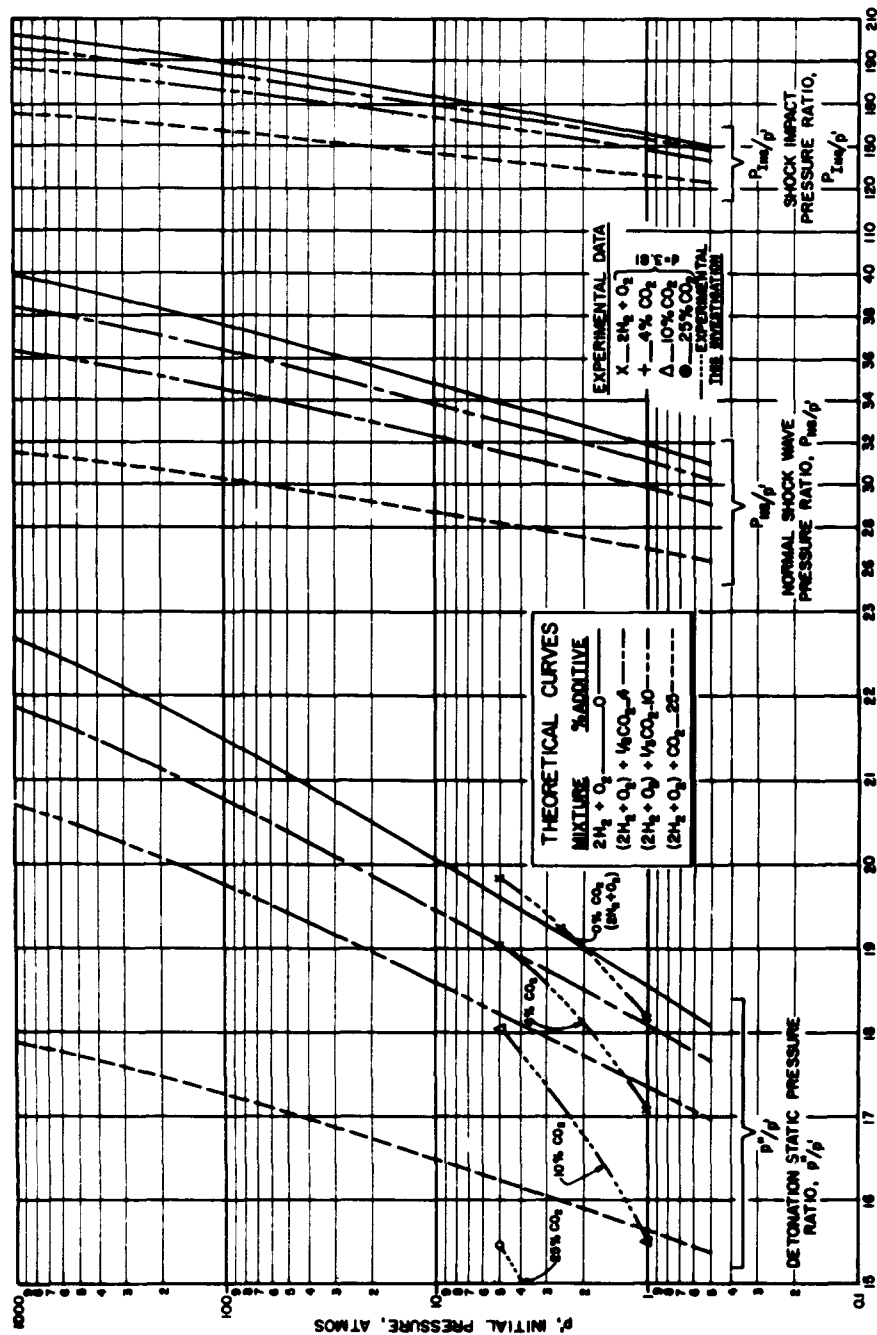


FIG. 10 VARIATION OF RATIOS OF DETONATION AND SHOCK WAVE PRESSURES TO INITIAL PRESSURE WITH INITIAL PRESSURE AT 300 °K INITIAL TEMPERATURE IN STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES ADMIXED WITH CARBON DIOXIDE.

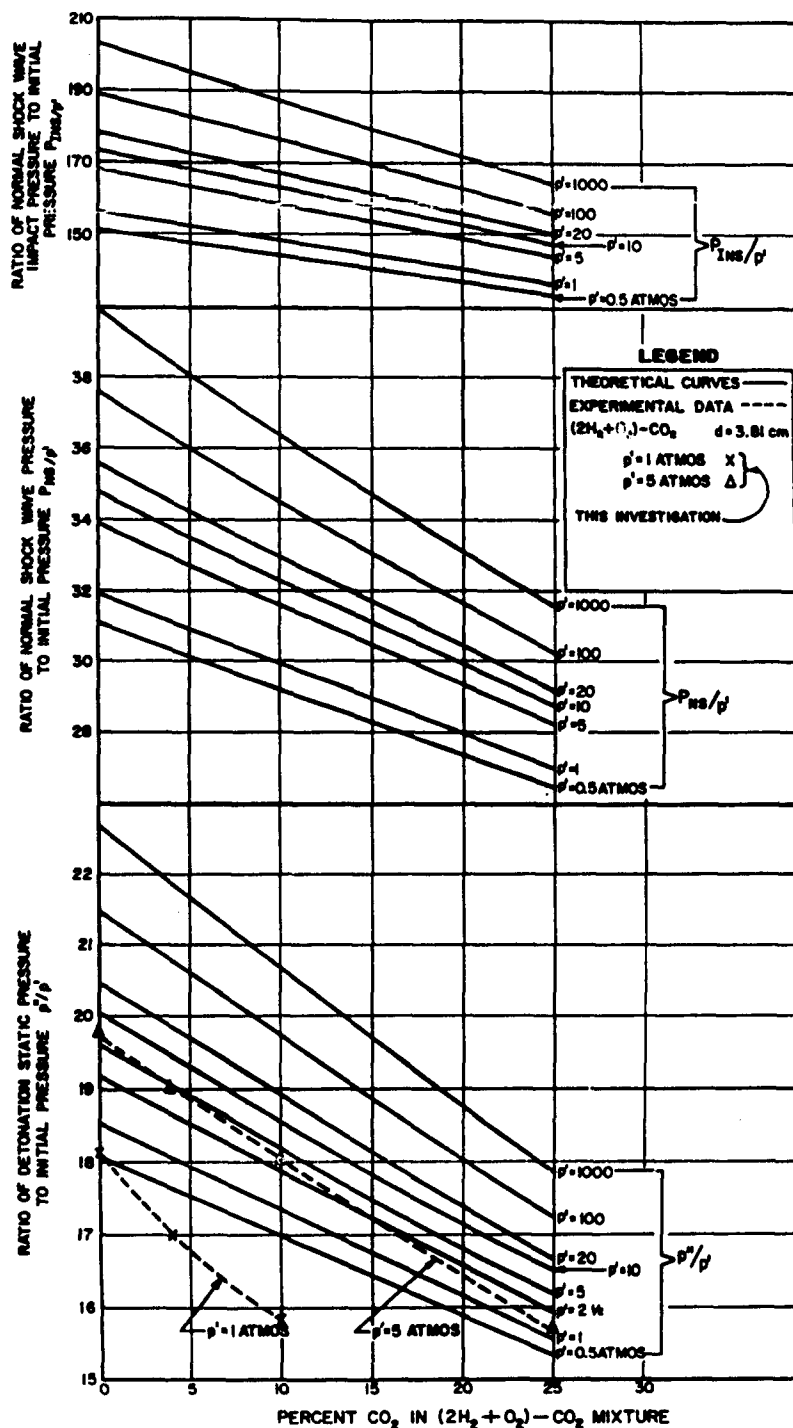


FIG. 1.1 VARIATION OF RATIOS OF DETONATION AND SHOCK WAVE PRESSURES TO INITIAL PRESSURE WITH PERCENT CARBON DIOXIDE IN STOICHIOMETRIC HYDROGEN-OXYGEN-CARBON DIOXIDE MIXTURES AT VARIOUS INITIAL PRESSURES AND INITIAL TEMPERATURE OF 300° K.

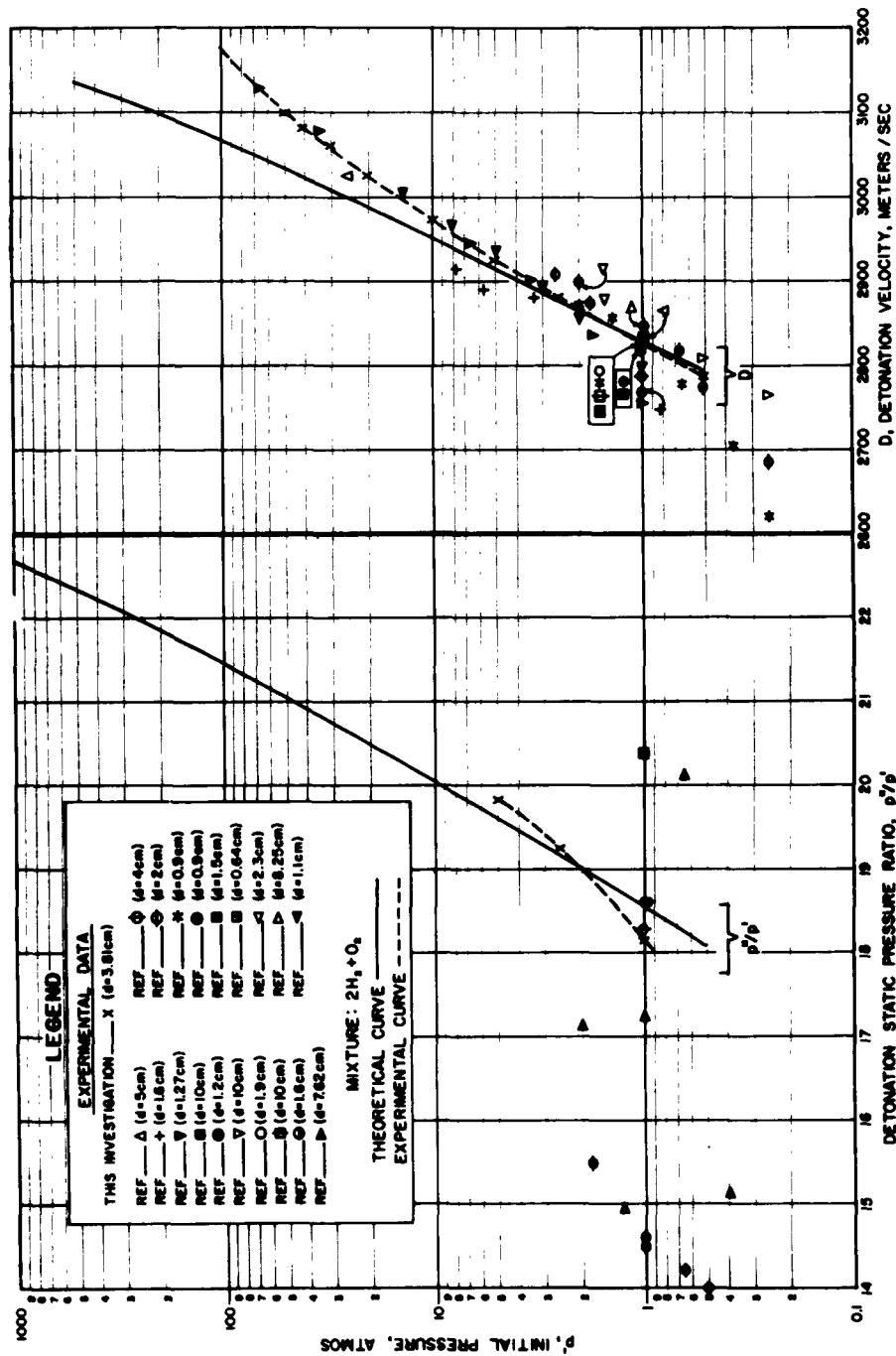
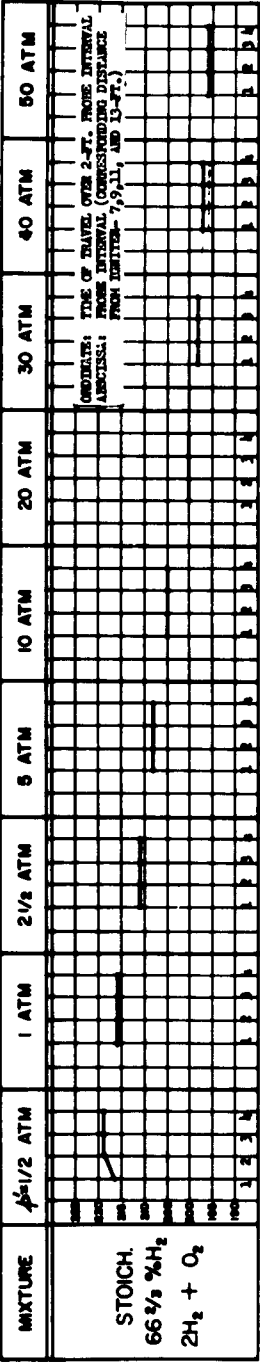


FIG. 1.2. VARIATION OF RATIOS OF DETONATION WAVE PRESSURE TO INITIAL PRESSURE AND DETONATION VELOCITY WITH INITIAL PRESSURE AT 300° K INITIAL TEMPERATURE IN STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES.



REPRESENTATIVE EXPERIMENTAL DETONATION VELOCITY DATA FOR THE STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURE  
 FIG. 4.3

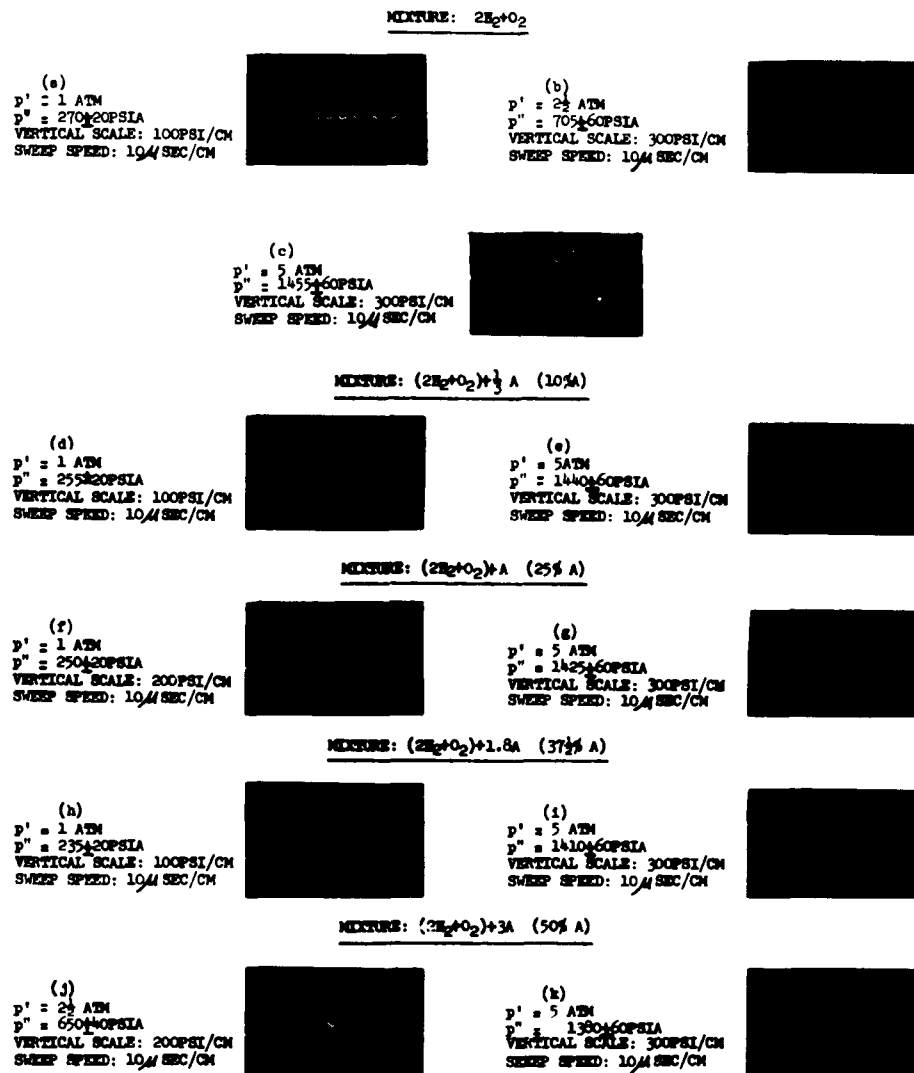


FIG 111 REPRESENTATIVE DETONATION STATIC PRESSURE-TIME OSCILLOGRAMS FOR STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES PURE AND ADDED WITH HELIUM, ARGON, OR CARBON DIOXIDE AT VARIOUS INITIAL PRESSURES AND AT 300°K INITIAL TEMPERATURE

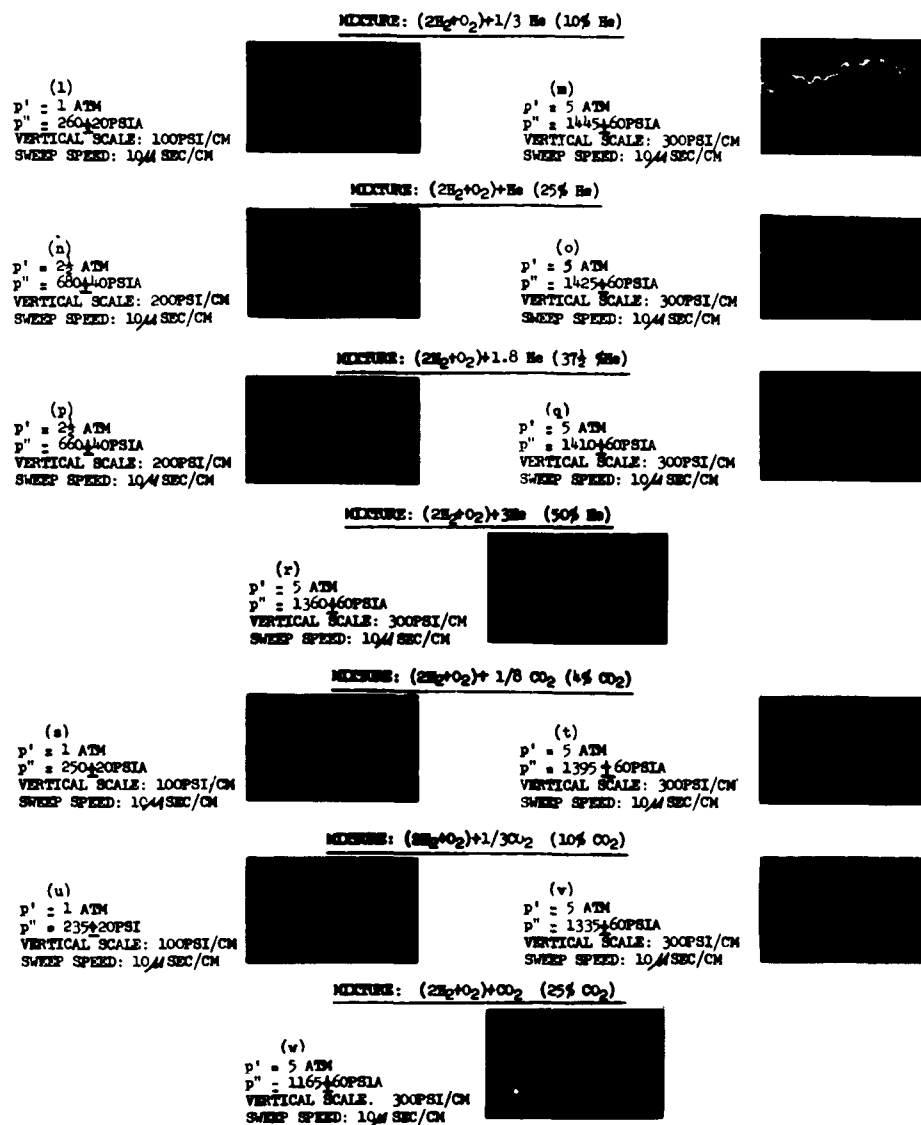


FIG 111 (CONT'D). REPRESENTATIVE DEFORMATION STATIC PRESSURE-TIME OSCILLOGRAMS FOR STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES PURE AND DILUTED WITH HELIUM, ARGON, OR CARBON DIOXIDE AT VARIOUS INITIAL PRESSURES AND AT 300°K INITIAL TEMPERATURE

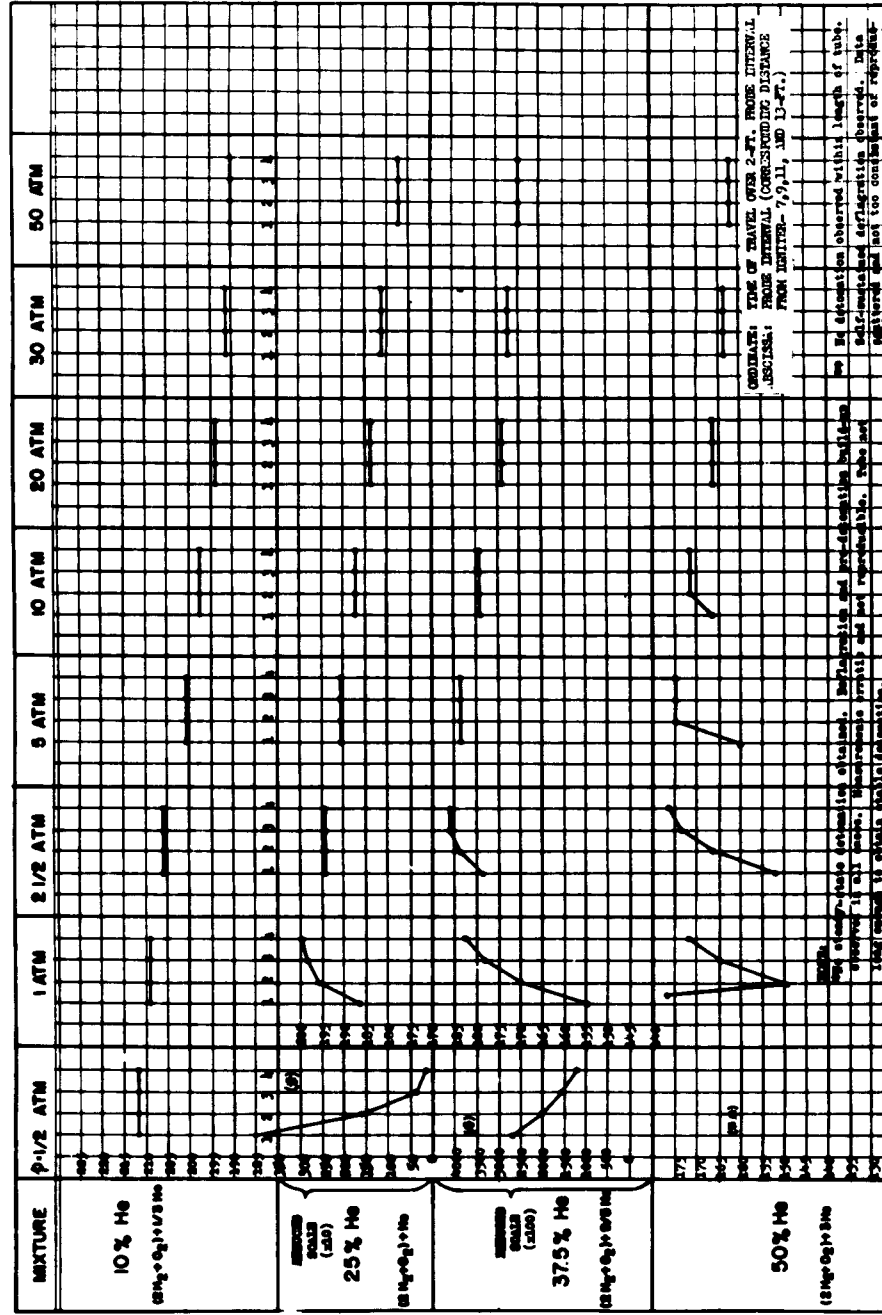


FIG. 4. REPRESENTATIVE EXPERIMENTAL DETONATION VELOCITY DATA FOR THE HYDROGEN-OXYGEN-HELIUM MIXTURES



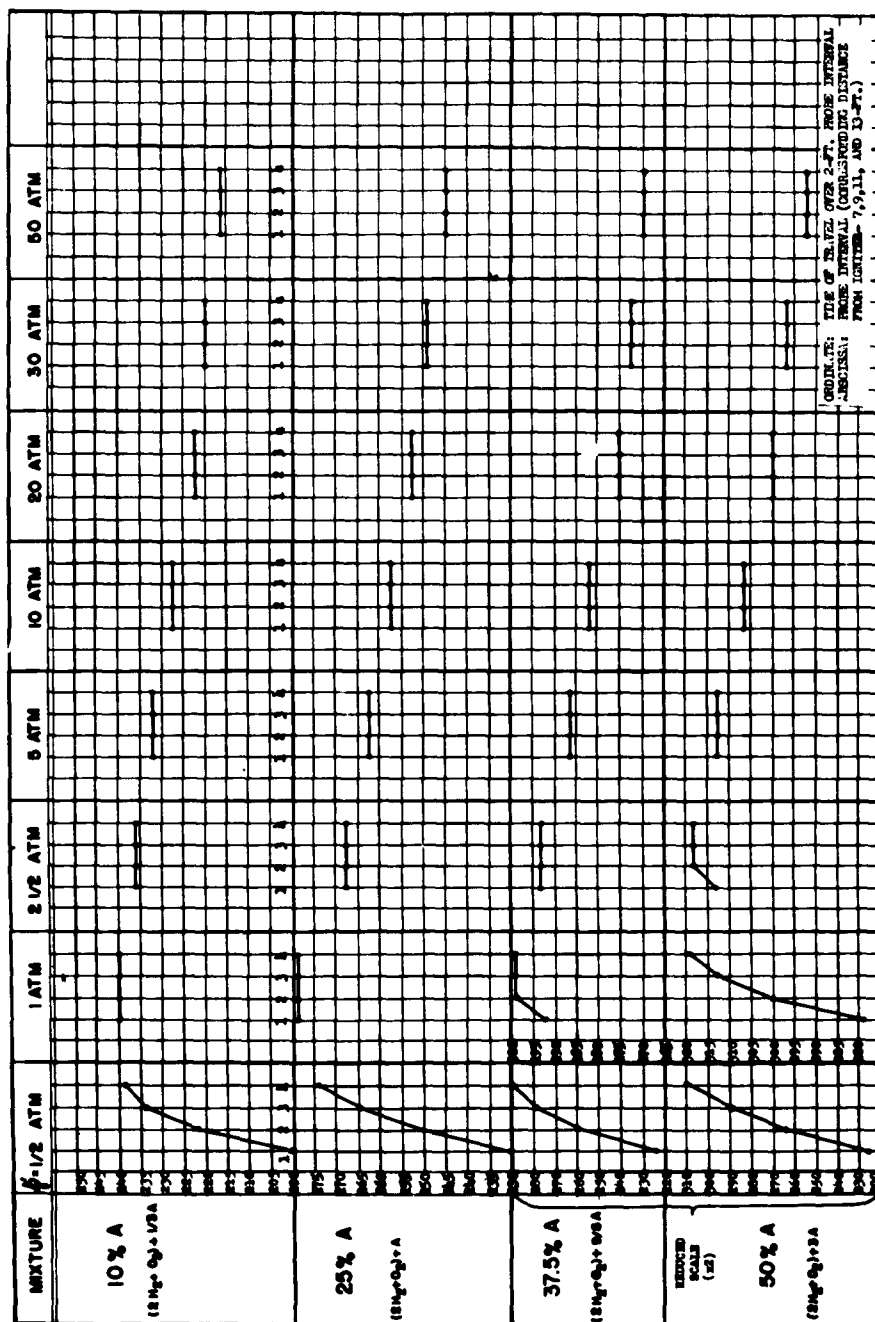


FIG. 4.6 REPRESENTATIVE EXPERIMENTAL DETONATION VELOCITY DATA FOR THE HYDROGEN-OXYGEN-ARGON MIXTURES

